IONIC SOLVATION IN AQUEOUS DIMETHYL SULFOXIDE

A Dissertation

Presented to

the Faculty of the Department of Chemistry

College of Arts and Sciences

University of Houston

In Partial Fulfillment

of the Requirements for the Degree

Doctor of Philosophy

---

by

C. Patrick Hagan

May 1972

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ABSTRACT

Enthalpies of solution of tetraphenylphosphonium bromide, sodium tetraphenylborate, sodium bromide, sodium iodide, sodium hydroxide, ethyl acetate, and tetra-n-butylammonium chloride, bromide, and iodide have been measured at 25° in water, DMSO, and seven water-DMSO mixtures. The enthalpy of solution of tetra-n-butyltin in DMSO has been measured. Enthalpies of solution of n-propyl tosylate in mixtures containing greater than 50% by volume DMSO were measured.

Using the enthalpy of transfer assumption $\Delta\Delta H[(C_6H_5)_4P^+] = \Delta\Delta H[^-B(C_6H_5)_4]$, $\Delta\Delta H$ values have been calculated for $(n\text{-}C_4H_9)_4N^+$, Na^+, ^-OH, Cl^-, Br^-, and I^- ions.

The significant trends in single ion $\Delta\Delta H$ values are (1) the tetra-n-butylammonium ion is desolvated by the addition of DMSO to water, the maximum desolvation being reached when the concentration of DMSO is about 65% by volume; (2) the sodium ion is initially slightly desolvated by the addition of DMSO to water, but the ion gains in solvation when the DMSO concentration begins to exceed about 30% by volume; (3) all of the anions are slightly more solvated by the addition of a small amount of DMSO to water. When the DMSO concentration exceeds about 30% by volume the anions are desolvated, the desolvation for hydroxide ion being quite pronounced.

The halide ions reach a maximum desolvation when the DMSO concentration is about 80% by volume.

The $\Delta\Delta H$ values for hydroxide ion and ethyl acetate have been used in conjunction with kinetic data from the literature to calculate $\Delta\Delta H$ values for the transition state of the base-catalyzed hydrolysis of ethyl acetate. The relative contributions of changes in anion, substrate, and transition state solvation upon addition of DMSO to water, to the observed changes in the rate of base-catalyzed hydrolysis of ethyl acetate are discussed.

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I

INTRODUCTION

INTRODUCTION

The rates of many organic reactions involving anions (e.g., SN_2, S_NAr, and elimination reactions) are greatly accelerated when the reaction medium is a dipolar aprotic solvent rather than a protic solvent [1]. Examples of some dipolar aprotic solvents are dimethyl sulfoxide (DMSO), N,N-dimethylformamide (DMF), and acetonitrile. Two major explanations [1] have been proposed to account for the observed rate enhancements. One explanation is that the reactants (especially the anions) are less solvated in dipolar aprotic solvents than in protic solvents. The other explanation is that the transition states for the reactions are more solvated in dipolar aprotic solvents than in protic solvents.

Obviously either or both of the two proposals could be responsible for the observed solvent effects on the rate of a bimolecular nucleophilic substitution reaction (Eq. 1).

$$Nu^- + RX \rightarrow [Nu\cdots R\cdots X]^{\ddagger -} \rightarrow NuR + X^- \qquad (1)$$

Parker [1] has used solvent activity coefficients to evaluate the relative importance of these two factors. The solvent activity coefficient, ${}^{o}\gamma_i^s$ is defined [2] such that it is proportional to the change in standard chemical potential, $\bar{u}_i^o$, of a solute upon transfer from an arbitrarily chosen

reference solvent, 0, to another solvent, S, at a temperature, T, (Eq. 2). Equation 3 shows to what extent rate changes,

$$\bar{u}_i^S = \bar{u}_i^o + RT \ln {}^o\gamma_i^S \qquad (2)$$

$$\log \frac{k^S}{k^o} = \log {}^o\gamma^S_{Nu^-} + \log {}^o\gamma^S_{RX} - \log {}^o\gamma^S_{\ddagger} \qquad (3)$$

upon transfer from a reference solvent, 0, to another solvent, S, are due to changes in solvation of reactant anion, log ${}^o\gamma^S_{Nu^-}$, of substrate, log ${}^o\gamma^S_{RX}$, and of transition state, log ${}^o\gamma^S_{\ddagger}$.

The solvent activity coefficients of non-electrolytes, log ${}^o\gamma^S_{RX}$, are readily obtained from solubility data in the two solvents of interest, or from distribution coefficients with a third immiscible solvent [1a]. The solvent activity coefficient for the transition state, log ${}^o\gamma^S_{\ddagger}$, is determined from equation 3 once the solvent activity coefficient for the nucleophile is known [1a].

Obviously it is impossible to determine the single ion solvent activity coefficient for the reactant nucleophile, log ${}^o\gamma^S_{Nu^-}$. While solvent activity coefficients for salts (MX) are available from solubility data [3], that part of the total activity coefficient that is due to the cation ${}^o\gamma^S_{M^+}$ and that part due to the anion ${}^o\gamma^S_{X^-}$ are not determinable. Two alternatives have been devised to circumvent this difficulty.

The first alternative [3] is to arbitrarily assign a value of unity to a cation or anion (e.g., X^-) as a reference ion. Pseudo-solvent activity coefficients, ${}_{X^-}{}^{o}\gamma^{s}_{M^+}$, relative to the reference ion ${}^{o}\gamma^{s}_{X^-}$, are calculated from equation 4

$$\log \frac{k^o}{k^s}(MX) = \log {}^{o}\gamma^{s}_{M^+} + \log {}^{o}\gamma^{s}_{X^-} = \log {}_{X^-}{}^{o}\gamma^{s}_{M^+} \quad (4)$$

using the solubility products of MX in the two solvents. Parker [3] has determined solvent activity coefficients for anions upon transfer from water to dipolar aprotic solvents using thiocyanate ion as the reference ion. Table I shows some of these values. A positive value indicates that the anion has been desolvated relative to SCN^- upon transfer from water to the second solvent.

The second, and more widely used alternative, makes use of certain extrathermodynamic assumptions to split activity coefficients into cation and anion parts.

One extrathermodynamic assumption is that if two ions of equal but opposite charge are of approximately the same size, and if the charge on the central atom of the ion is well shielded or highly delocalized so that there is little charge density on the surface of the ion, then the solvent activity coefficient for transfer from one solvent to another will be the same for the cation and the anion. Some examples of these equivalent ions are the following:

TABLE I

Log $_{SCN^-}{}^{w}\gamma^{s}_{X^-}$ (Reference Solvent: Water at 25°) [3]

Anion	MeOH	DMF	DMSO
SCN^-	0	0	0
Cl^-	1.3	5.1	5.4
Br^-	0.9	3.1	3.1
I^-	0.3	0.2	0.2
$AgCl_2^-$	-1.7	-1.2	-0.3
AgI_2^-	-1.2	-6.6	-5.7

a) ${}^{o}\gamma^{s}\ (C_6H_5)_4As^+ = {}^{o}\gamma^{s}\ {}^-B(C_6H_5)_4$ (4-6)

b) ${}^{o}\gamma^{s}\ (C_6H_5)_4P^+ = {}^{o}\gamma^{s}\ {}^-B(C_6H_5)_4$ (7)

c) ${}^{o}\gamma^{s}\ (\underline{n}\text{-}C_4H_9)_4N^+ = {}^{o}\gamma^{s}\ {}^-B(\underline{n}\text{-}C_4H_9)_4$ (8)

d) ${}^{o}\gamma^{s}\ (\underline{i}\text{-amyl})_3N^+(\underline{n}\text{-}C_4H_9) = {}^{o}\gamma^{s}\ {}^-B(C_6H_5)_4$ (6,9)

Another extrathermodynamic assumption is that the solvent activity coefficients of a neutral species and of an ion are equal provided the two are of similar size and shape, and the surface charge density on the ion is small. Some examples are the following:

a) ${}^{o}\gamma^{s}\ {}^-B(C_6H_5)_4 = {}^{o}\gamma^{s}(C_6H_5)_4C$ (7).

b) ${}^{o}\gamma^{s}I_2 = {}^{o}\gamma^{s}I_3^-$ (2,6)

c) ${}^{o}\gamma^{s}\text{Ferrocene} = {}^{o}\gamma^{s}\text{Ferricinium}^+$ (11)

d) ${}^{o}\gamma^{s}\text{ArX} = {}^{o}\gamma^{s}\text{ArXY}^{\ddagger}$ (2,10)

(where ArX = unchanged aromatic substrate,
and $\text{ArXY}^{\ddagger}$ = S_NAr transition state)

For many reactions it is a decrease in enthalpy of activation rather than an increase in entropy of activation that is primarily responsible for the observed rate enhancements upon transfer from protic to dipolar aprotic solvents [1a,1b]. Also the change in enthalpy of solvation

of the reactant anion is usually more important than the change in enthalpy of the neutral molecule [20]. Table II compares the change in enthalpy and entropy of activation corresponding to the change in free energy of activation for the appropriate reaction to the change in chemical potential of the reactant anion upon solvent transfer [1a]. Table II shows that the change in free energy of activation of the appropriate reaction is primarily due to the change in enthalpy of activation. The change in enthalpy of activation is approximately equal to the change in free energy of solvation of the anion. Thus, most of the effect of solvent transfer on the reaction rate is due to changes in the enthalpy of solvation of the reactant anion. Parker [20] has also pointed out that $[\Delta\Delta H_s(Et_4NX) - \Delta\Delta H_s(Et_4NI)]$[4] for transfer of the tetraethylammonium halides is almost identical with $[\Delta\Delta G(AgX) - \Delta\Delta G(AgI)]$ for transfer of the silver halides [3] from water to DMSO at 25°.

Single ion enthalpies of transfer for ions are calculated from calorimetrically measured heats of solution for salts in the two solvents. The same extrathermodynamic assumptions employed for the determination of single ion solvent activity coefficients are used to split enthalpies of transfer for salts into cation and anion contributions. Solvent effects on the transition state for a reaction can

TABLE II

PROTIC-DIPOLAR APROTIC SOLVENT EFFECTS ON ENTHALPY AND ENTROPY OF ACTIVATION[a]

FOR BIMOLECULAR REACTIONS AT 25°. (Reference Solvent: Methanol)

Reactants RX + Nu^-	Reaction Type	$\frac{\Delta H_o^{\ddagger} - \Delta H_s^{\ddagger}}{2.303R\ 298}$	$\frac{\Delta S_o^{\ddagger} - \Delta S_s^{\ddagger}}{2.303R}$	$\frac{\Delta G_o - \Delta G_s}{2.303R\ 298}$ (Nu^-)
$CH_3Cl + N_3^-$ [b]	S_N2	4.3	1.0	4.9
$CH_3Cl + SCN^-$ [b]	S_N2	2.8	1.4	2.7
$CH_3I + SCN^-$ [b]	S_N2	3.2	1.0	2.7
$4\text{-}NO_2C_6H_4F + N_3^-$ [b]	S_NAr	3.5	-0.9	4.9
$2,4\text{-}(NO_2)_2C_6H_3I + Cl^-$ [b]	S_NAr	6.2	-0.3	6.5
$2,4\text{-}(NO_2)_2C_6H_3Cl + SCN^-$ [b]	S_NAr	2.2	0.2	2.7
$2\text{-}NO_2C_6H_4Cl + OMe^-$ [c]	S_NAr	2.9	-0.3	4.0
$C_6H_5CH_2Cl + OMe^-$ [c]	S_N2	3.7	1.3	4.0

[a]Data from 1a. [b]S = DMF. [c]S = 80% V:V DMSO-methanol

can be determined from equation 5 [21], where $\Delta\Delta H_s^t$ is the

$$\Delta\Delta H_s^t = \Sigma\ \Delta\Delta H_s + \Delta\Delta H^{\ddagger} \qquad (5)$$

enthalpy of transfer for the transition state, $\Sigma\ \Delta\Delta H_s$ is the sum of the enthalpies of transfer for the reactants, and $\Delta\Delta H^{\ddagger}$ is the transfer value for the enthalpy of activation. Haberfield [8] has determined enthalpies of transfer of some SN_2 and S_NAr transition states from methanol to DMF, and has concluded that desolvation of the reactants (in particular the reactant nucleophile) is not always the governing factor in determining rate enhancements. In some cases [8] the change in solvation of the transition state is far greater than the change in solvation of the reactants upon solvent transfer.

Indeed the validity of the extrathermodynamic assumptions used to obtain single ion solvent activity coefficients and enthalpies of transfer can never be unequivocally demonstrated. But to the extent that various assumptions give approximately equivalent values for single ion activity coefficients and single ion enthalpies of transfer; and to the extent that different assumptions lead to the same qualitative conclusions about the relative solvation of ions in different solvents, the assumptions are useful. Fuchs and Rodewald [22] have determined the single ion enthalpies of transfer for

thirteen ions from methanol to four other solvents using the assumptions:

a) $\Delta\Delta H_s(\underline{n}\text{-}C_4H_9)N^+ = \Delta\Delta H_s\ ^-B(\underline{n}\text{-}C_4H_9)_4$,

b) $\Delta\Delta H_s(\underline{n}\text{-}C_5H_{11})N^+ = \Delta\Delta H_s\ ^-B(\underline{n}\text{-}C_5H_{11})_4$,

c) $\Delta\Delta H_s(C_6H_5)_4As^+ = \Delta\Delta H_s\ ^-B(C_6H_5)_4$.

In all cases there is good agreement between single ion values of transfer obtained from the first two assumptions, but values obtained from the tetraphenylarsonium tetraphenylborate assumption show deviations. The authors point out that the deviations probably do not result from the validity of the assumption itself, but from the fact that the concentration dependence of the enthalpy of solution of sodium tetraphenylborate in methanol requires that the enthalpy of solution at infinite dilution be determined by extrapolation. The extrapolated value is probably in error.

Single ion solvent activity coefficients and enthalpies of solvent transfer have provided much information about the relative solvation of ions in protic and dipolar aprotic solvents. It has been shown that water is better able to solvate small, densely charged anions than large anions [4-6, 23]. For example, the order of solvation of the halide ions in water is $Cl^- > Br^- > I^-$ [4,24]. Protic solvents are highly structured

because of hydrogen bonding. Since small anions are good hydrogen bond acceptors, they interact strongly with protic solvents. In the transfer from water to DMSO the small anions chloride and bromide are desolvated, while the larger, more polarizable iodide anion actually gains in solvation [24]. Thus DMSO is better able to solvate large anions than is water. One might expect that upon transfer from water to DMSO the order of halide ion solvation would be reversed. Fuchs and coworkers [24] have shown that this is not the case. The order of solvation of the halide ions in DMSO is still $Cl^- > Br^- > I^-$ but the <u>difference</u> in the extent to which they are solvated is greatly diminished in DMSO.

Cations are not hydrogen bond acceptors. The main forces responsible for their solvation are ion-dipole interactions [1c]. Small, highly charged cations are more strongly solvated by dipolar aprotic solvents than by water [25]. Large "organic" cations [Bu_4N^+, $(C_6H_5)_4As^+$] are also more solvated by dipolar aprotic solvents than by water [1a].

Yao and Bennion [26,27], from transport behavior and viscosity studies of ions in DMSO at 25°, have reached the following conclusions about the interactions of ions with DMSO:

a. Spherically symmetrical ions, such as (<u>iso</u>-amyl)$_3$BuN$^+$ and $^-B(C_6H_5)_4$, with weak surface charge interact (ion-dipole

interaction) only weakly with DMSO. The ion-dipole interaction is approximately equal to the DMSO dipole-dipole interaction and hence the ions are poorly solvated by DMSO.

b. Small densely charged ions (e.g., Li^+, Na^+, K^+) interact strongly with the solvent dipole. The ion-dipole interaction energy for Na^+ is at least six times the DMSO-DMSO dipole-dipole interaction. The studies indicate that Li^+, Na^+, and K^+ ions are solvated with about five, three, and three DMSO molecules, respectively. The halide anions are only slightly solvated by DMSO and their solvation is in the order $Cl^- > Br^- > I^-$ indicating that perhaps ion-dipole interactions are also important in small anion solvation.

c. Anions of about the same size and geometry as the DMSO molecules, with or without weak dipoles, (e.g., ClO_4^-) fit well into the pyramidal DMSO structure. Due to dipole-induced dipole interactions, there is competition between DMSO molecules in the vicinity of the ions to arrange themselves about the ions. The net result of this arrangement is an increase in solvent structure by the formation of a solvent sheath about the ions, and a decrease in solvent structure caused by the weakening of adjacent solvent-solvent interactions.

d. Ions of about the same size as DMSO but of dissimilar shape and weak permanent dipoles (SCN^-, $CF_3SO_3^-$) interact only weakly with the DMSO dipole.

Yao and Bennion [26] also found that at 25° $NaClO_4$, NaSCN, and $NaB(C_6H_5)_4$ are slightly associated in DMSO. The salts CH_3SO_3Na and $(\underline{iso}\text{-amyl})_3BuNB(C_6H_5)_4$ are associated in DMSO and their respective association constants are 100 and 12.

Maxey and Popov [28] have found that the low frequency infrared vibrational absorption bands of $LiClO_4$, NH_4SCN, and $NaB(C_6H_5)_4$ in DMSO solution are independent of the nature and mass of the anion. This observation indicates that the solvent dipoles are oriented with the oxygen atom in direct proximity to the metal, and that there is not sufficient interaction between DMSO molecules and the anions to be observed by infrared spectroscopy.

Neutral molecules, especially if they are large and polarizable (e.g., nitro aromatics) are often a great deal more solvated in dipolar aprotic solvents relative to water [1a]. Molecules containing large alkyl chains (e.g., alkyl halides) are not appreciably more solvated by DMSO than by water. Because ions have greater solvation energies than non-electrolytes, solvation changes in neutral molecules are sometimes overlooked when considering the factors responsible for rate enhancements. Since it is solvation <u>differences</u> that are important, solvation changes of the reactant neutral molecule should always be considered.

The discovery that large polarizable anions are better solvated by dipolar aprotic solvents than by protic solvents led to the logical conclusion that many transition states for bimolecular reactions should also be better solvated by dipolar aprotic solvents. That this often is the case has been shown by Parker [1a]. In general the large and polarizable S_NAr transition states are more solvated by dipolar aprotic solvents while protic solvents are better solvents for small anionic transition states.

Because small anions are strongly desolvated in dipolar aprotic solvents, it is often difficult to find a sufficiently soluble electrolyte to serve as a nucleophile source. In these situations mixtures of dipolar aprotic-protic solvents are extremely useful. Mixtures of DMSO with water or alcohols have been the most frequently used.

The rate enhancements for bimolecular reactions characteristic for transfers from protic to dipolar aprotic solvents are observed in modified form for transfers from protic to dipolar-aprotic solvent mixtures. Murto [12] found that at 25° added DMSO has a strong rate accelerating effect on the hydroxide ion-catalyzed hydrolysis of methyl iodide, and on the methoxide and ethoxide ion-catalyzed alcoholysis of methyl iodide. In pure DMSO the reaction rate is approximately 10^6-10^7 times faster than in water, 2.5×10^5 times the rate

in methanol, and 2.9 x 10^4 times the rate in ethanol. The rate increases are attributed to a decrease in the activation energy for the reaction with added DMSO. The log A value for the alcoholysis reaction varies relatively slightly with added DMSO, but for the hydrolysis reaction log A decreases with added DMSO. The log A decrease should decrease the reaction rate in DMSO relative to water, but the rate increase is due to a quite pronounced simultaneous decrease in the activation energy.

Benzyl chlorides undergo a decrease in the rate of uncatalyzed hydrolysis with added DMSO [29], but the decrease is less in aqueous DMSO mixtures than in aqueous acetone, dioxane, or ethanol. The decrease in the reaction rate is related to the decrease in water content of the solvent mixture with increasing DMSO. The displacement of chloride ion from benzyl chlorides by hydroxide ion [16] shows an increase in the rate of the reaction with added DMSO. Added acetone causes a decrease in the reaction rate. The opposite effects of acetone and DMSO on the reaction rate are attributed to differences in transition state solvation in aqueous acetone relative to aqueous DMSO.

The alkaline hydrolysis of ethyl acetate in aqueous DMSO has been investigated by Tommila and Murto [30]. The reaction is accelerated upon addition of DMSO especially at

high DMSO concentrations. The authors attribute the rate enhancements to increased activity of the hydroxide ion with addition of DMSO to the solvent. The enthalpy and entropy of activation both decrease slightly until the mole fraction of DMSO is about 0.28. At higher mole fractions of DMSO both increase quite rapidly. The free energy of activation undergoes a gradual decrease with increasing DMSO.

Roberts [31] investigated the effect of added DMSO on the alkaline hydrolysis of straight-chain and branched-chain esters. Rate constant increases are proportional to DMSO concentration (0.20-0.65 mole fraction DMSO) over the entire solvent composition range. The reaction rates for straight-chain esters show enhanced sensitivity to DMSO concentration in solvent compositions containing a molar excess of DMSO. The results are interpreted in terms of the importance of steric bulk to solvation in aqueous DMSO. The increased solvation of the transition state, not the desolvation of the hydroxide ion, by DMSO is believed to be responsible for the rate enhancements.

Haberfield [32] has measured the enthalpy of transfer of reactants, and transition states, for the base-catalyzed saponifications of ethyl acetate, ethyl benzoate, iso-propyl benzoate and tert-butyl benzoate in aqueous DMSO and aqueous

ethanol. Haberfield has concluded that the desolvation of the transition state is less than the desolvation of the reactants, and this is responsible for the enhanced reaction rates.

A number of authors have investigated the nature of aqueous DMSO solutions. Lindberg and Kenttamaa [33], and Cowie and Toporowski [34] have attributed the deviations from ideality of viscosity, density, refractive indices, and enthalpies of mixing for water containing various amounts of DMSO, to association interactions between water and DMSO. These interactions are at a maximum when the molar DMSO-water ratio is 2:1.

Evidence has been presented [35,36] that hydrogen bonding between two water molecules is not as strong as hydrogen bonding between a water molecule and a DMSO molecule. Drinkard and Kivelson [37] do not agree with this idea. They conclude from NMR shifts of the hydroxyl protons relative to the DMSO methyl protons, that water hydrogen bonds to itself more strongly than to DMSO. Pulsed NMR studies [38] of the relaxation times of protons indicate a minimum of molecular mobility (both rotational and translational) at approximately 0.65 mole fraction of water. The data, as well as data from neutron inelastic scattering and x-ray experiments [36], have been interpreted to mean that addition of small amounts (up

to 20 mole percent) of DMSO to water increases the water structure. Water-water hydrogen bonds are "rigidified" rather than being broken. At higher concentrations of DMSO the water structure is broken down due to DMSO-water interactions. A recent study of the partial molar enthalpies of solution of water and DMSO in their mixtures [39] supports the hypothesis that small amounts of water destroy DMSO structure while small amounts of DMSO promote water structure.

Since halide ions are strongly solvated in water due to hydrogen bonding, it might be expected that in aqueous DMSO the halide ions would be preferentially solvated by the water. Langford and Stengle [40] have presented evidence that this is not the case. Studies of $^{35}Cl^-$ NMR chemical shifts in aqueous acetonitrile and aqueous DMSO indicate that there is equal solvation of the chloride ion by water and the dipolar aprotic solvent in the mixtures. The chemical shifts were measured as a function of the DMSO or acetonitrile content over the entire solvent composition range.

Further information about the solvation of anions in aqueous DMSO has come from the use of this solvent to measure acidity functions [41-43]. The acidity function, H_-, is defined [44] by equation 6 where a_{H^+} is the hydrogen ion activity in the solution

$$H_- = \log (a_{H^+} fA/fHA) \qquad (6)$$

and f is the activity coefficient of the indicator. When the activity coefficients of the indicator approach unity, and when the activity of the hydrogen ion becomes equal to its concentration (dilute solutions), the acidity function becomes identical with pH. The acidity function of a solution is a measure of the ability of that solution to remove a proton from an acid. Once the acidity function for a solution is known the solution can be used to measure the acidities of very weak acids.

Aqueous DMSO solutions containing an anion are extremely powerful kinetic base systems. As DMSO is added to protonic solvents containing an anion the H_- value of the solvent increases dramatically due to the increased activity of the anion [40-43]. Table III [42] shows the effect of added DMSO on the H_- function. It should be noted that sizable increases in the acidity function occur even at low concentrations of DMSO. Apparently the activity of the anion is increased not only because of displacement of water, but also because the DMSO effectively "ties up" the remaining water [42]. The H_- value for a 0.01 M tetraethylammonium hydroxide solution in 50 mole percent DMSO is 17.2 (Table III). Thus, the solution is about 10^4 times as basic as the purely aqueous solution. However, the molar ratio of water to hydroxide ion is still high, being about 280.

TABLE III [42]

H_- FUNCTION IN AQUEOUS DMSO CONTAINING 0.011 M Me_4NOH

Mole % DMSO	H_-	Mole % DMSO	H_-
0	--	50	17.23
1	--	55	17.60
5	12.18	60	17.93
10	12.94	65	18.40
15	13.63	70	18.87
20	14.28	75	19.3
25	14.86	80	19.9
30	15.40	85	20.5
35	15.92	90	21.3
40	16.41	92.5	21.9
45	16.84	95	22.5

In spite of the recent interest in the effect of protic-dipolar aprotic solvent mixtures on reaction rates, relatively little information has appeared in the literature concerning the effect of these solvent mixtures on the solvation of ions. Fuchs and Plumlee [45] have found that solvation of the halide ions in DMSO is only slightly affected by the addition of water up to the composition $DMSO \cdot H_2O$. Tetrabutylammonium ion and propyl tosylate were desolvated. Their work covered only a limited range of DMSO-water mixtures.

The present study was carried out in order to determine the relative solvation of ions over the entire water-DMSO solvent composition range, and to determine to what extent the enhanced rates of base-catalyzed saponification of ethyl acetate in water-DMSO mixtures are due to changes in solvation of the reactants and changes in solvation of the transition state.

II

THE PRESENT STUDY

THE PRESENT STUDY

The present study makes use of the tetraphenylphosphonium tetraphenylborate assumption to calculate the enthalpies of transfer from water to water-DMSO mixtures of $(C_6H_5)_4P^+$, $^-B(C_6H_5)_4$, Bu_4N^+, Na^+, Cl^-, Br^-, I^-, and ^-OH ions. The enthalpies of transfer for ethyl acetate are also determined. The heat of solution of n-propyl tosylate in water, 15%, 30%, and 50% (vol/vol) DMSO is measured. The heat of solution of tetra-n-butyltin in DMSO is also measured.

The results of the enthalpies of transfer for hydroxide ion and ethyl acetate are used to determine to what extent the acceleration of the rate of base-catalyzed hydrolysis of ethyl acetate upon addition of DMSO is due to changes in solvation of the reactants and of the transition state.

The single ion enthalpies of transfer are plotted versus solvent composition.

III

EXPERIMENTAL

EXPERIMENTAL

A. PREPARATION AND PURIFICATION OF CHEMICALS

1. Dimethyl Sulfoxide

The dimethyl sulfoxide was "Baker Analyzed" reagent grade listed as containing 0.04% water. The DMSO was dried further by storing over 4A molecular sieve. The aqueous DMSO mixtures were prepared volumetrically with distilled water.

2. Tetraphenylphosphonium Bromide

Tetraphenylphosphonium bromide was obtained from Alfa Inorganics. The salt was dissolved in a small amount of iso-propyl alcohol. Addition of about 9 volumes of acetone failed to cause the salt to precipitate. Addition of an equal volume of benzene caused the salt to precipitate. The salt was vacuum dried at 100°. The melting point was 297-298.5°.

3. Sodium Tetraphenylborate

Sodium tetraphenylborate was obtained from Aldrich Chemical Company. It was vacuum dried at 100° for 24 hours.

4. Sodium Bromide and Sodium Iodide

Sodium bromide and sodium iodide were obtained from Fisher Scientific Company and dried under vacuum at 100° for 24 hours.

5. Sodium Hydroxide

The sodium hydroxide (assay 99%) was obtained from Matheson Coleman & Bell. The sealed bottle of sodium hydroxide was opened in a nitrogen filled dry box. The sodium hydroxide was pulverized and transferred under nitrogen atmosphere to a drying vessel. After drying under vacuum at 100° for 24 hours the sodium hydroxide was transferred under vacuum to the dry box.

6. Tetra-n-butylammonium Chloride

Wet tetra-n-butylammonium chloride was obtained from Eastman Organic Chemicals. The salt had been previously recrystallized and dried [46]. The salt was dissolved in methylene chloride and the solution dried over 3A molecular sieve. The volatile solvent was removed and the salt dried under vacuum for 24 hours.

7. Tetra-n-butylammonium Bromide

Tetra-n-butylammonium bromide was obtained from Eastman Organic Chemicals. It was dried under vacuum at 50° for 24 hours.

8. Tetra-n-butylammonium Iodide

Tetra-n-butylammonium iodide was obtained from Eastman Organic Chemicals and recrystallized from a benzene-heptane

mixture. The recrystallized salt was dried under vacuum at 50° for 24 hours.

9. n-Propyl Tosylate

The preparation of n-propyl tosylate has been previously described [26]. It was distilled at 1 mm, boiling point 120-121°.

10. Tetra-n-butyltin

Tetra-n-butyltin was obtained from Alfa Inorganics. It was distilled at 11 mm, boiling point 154-155°.

11. Ethyl Acetate

Ethyl acetate was "Baker Analyzed" reagent grade. It was not further purified.

B. CALORIMETRY

The calorimeter was an all-glass system with a total volume of 100 ml. The body (but not the top) was vacuum jacketed and silvered. The removable top was fitted with ground-glass joints to hold a resistance heater, thermistor probe, and sample holder. For solid samples two types of sample delivery devices were used. Some samples were weighed into glass bulbs and mounted on the sample holder with rubber tubing. All sodium hydroxide samples were weighed into glass bulbs. Most of the other solid samples were weighed into a

device consisting of a short piece of glass tubing to which a polyethylene cap was fitted. The cap was attached to the glass tubing with a polypropylene thread. The device was attached to the sample holder and a closely fitting polypropylene rod was inserted. The calorimeter, with 70 ml. of solvent, was submerged in a constant temperature bath ($25.000 \pm 0.004°$) and allowed to equilibrate while the solvent was magnetically stirred. After thermal equilibration was attained (as indicated by the recorder baseline slope) the glass rod or polypropylene rod was depressed breaking the bulb and dislodging the polyethylene cap, introducing the sample near the bottom of the vessel. All liquid samples except ethyl acetate were weighed into glass bulbs.

Ethyl acetate did not give reproducible results when the samples were weighed into glass bulbs or the polyethylene capped device. Apparently the devices were not tight enough to avoid loss due to the volatility of ethyl acetate. Consequently, the ethyl acetate was introduced into the calorimeter from a microliter syringe. Reproducible results were obtained using this method. The weight of ethyl acetate was calculated from its density at 25°.

The heat of solution of the sample is measured using the thermistor which sends an out of balance signal through a Wheatstone bridge, to a digital multimeter (Keithly Instru-

ments Model 160). The signal is then fed through a voltage divider and finally into a recorder. The recorder deflection is calibrated by passing a known current (Sargent-Welch coulometric current source) through a heater of known resistance for a measured amount of time.

All samples were weighed on a Sartorius microbalance in a dry box containing a prepurified nitrogen atmosphere. The nitrogen was circulated periodically each day through 4A molecular sieve and drierite traps to remove moisture. To check for concentration effects for a given salt in any solvent several samples of the salt were dissolved in the solvent without renewing it. No concentration effects for any salt in any solvent were detected. As much as possible the sample sizes were weighed such that the concentration of the salt in 70 ml. of solvent was between 1×10^{-4}M and 5×10^{-4}M. In the case of salts with a low molecular weight and/or a small enthalpy of solution, this concentration range had to be exceeded. The table below shows the weight of each salt corresponding to the concentrations mentioned above.

The calorimeter was calibrated by measuring the enthalpy of solution of potassium chloride. The average value obtained is in good agreement with the value of 4.115 kcal $mole^{-1}$ reported by the National Standards Reference

WEIGHT OF SALT CORRESPONDING TO 1×10^{-4}M AND 5×10^{-4}M SOLUTION IN 70 ML. OF SOLVENT

Salt	MW	1×10^{-4}M wt. (mg)	5×10^{-4}M wt. (mg)
$(C_6H_5)_4PBr$	418	5.9	30
$NaB(C_6H_5)_4$	349	5.0	25
NaBr	103	1.5	7.5
$(\underline{n}\text{-}C_4H_9)_4NCl$	274	3.8	19
$(\underline{n}\text{-}C_4H_9)_4NBr$	318	4.5	23
$(\underline{n}\text{-}C_4H_9)_4NI$	449	6.4	32
$(\underline{n}\text{-}C_3H_7)OTs$	214	3.1	15
$(\underline{n}\text{-}C_4H_9)_4Sn$	347	4.9	25
EtOAc	88.1	1.3	6.5
NaOH	40	0.57	2.8

Data System NRSDS-NBS 2. The calibration data is shown in the table below.

ENTHALPY OF SOLUTION OF KCl

KCl (mg.)		ΔH_s
12.00		4.10
11.27		4.24
10.50		4.16
	Avg.	4.16 ± 0.05

C. CALCULATION OF THE ENTHALPY OF SOLUTION

$$\Delta H_s(\text{kcal mole}^{-1}) = I^2 \times R \times t \times \frac{d_c}{d_s} \times \frac{1 \text{ cal}}{4.184 \text{ joule}} \times \frac{\text{MW salt}}{\text{samp.wt.mg.}}$$

where:

I = calibration current (amp)

R = heater resistance (ohm)

t = calibration heating time (sec.)

d_s = sample recorder deflection

d_c = calibration recorder deflection

IV

RESULTS

RESULTS

In the following tables all sample weights are expressed in milligrams, all enthalpies of solution are expressed in kcal/mole, and all solvent mixtures are volume percent. The asterisk (*) indicates the point at which fresh solvent was introduced into the calorimeter. All values between asterisks were successive determinations in the same solvent. The volume of solvent was 70 ml. for all determinations.

TABLE IV

ENTHALPIES OF SOLUTION

Solvent: Water

$(C_6H_5)_4PBr$		$NaB(C_6H_5)_4$		NaBr	
Wt. (mg)	ΔH_s	Wt. (mg)	ΔH_s	Wt. (mg)	ΔH_s
13.25*	1.85	23.17*	-4.52	31.64*	- .13
14.55	1.85	23.29	-4.49	50.48	- .11
14.00	1.76	12.45	-4.58	34.06	- .14
15.23	1.95	12.18*	-4.62	24.27	- .12
8.58*	2.01	13.69	-4.53	25.28*	- .14
7.16	1.79			28.67	- .12
21.68	1.86				
25.37*	2.07				
21.57*	2.04				
17.86	1.95				
29.50	2.01				
34.32*	2.05				

TABLE IV CONTINUED

ENTHALPIES OF SOLUTION

Solvent: Water

$(n\text{-}C_4H_9)NCl$		$(n\text{-}C_4H_9)_4NBr$		$(n\text{-}C_4H_9)_4NI$	
Wt. (mg)	ΔH_s	Wt. (mg)	ΔH_s	Wt. (mg)	ΔH_s
22.94*	-7.46	14.12*	-1.99	19.19*	4.00
11.47*	-7.33	16.00	-2.02	24.62	4.06
4.99	-7.30	11.74	-2.07	23.74	4.14
11.11	-7.56	10.04*	-2.05	23.12	4.13
				24.30*	3.92

NaOH		NaI		EtOAc	
Wt. (mg)	ΔH_s	Wt. (mg)	ΔH_s	Wt. (mg)	ΔH_s
3.89*	-10.9	40.01*	-1.78	8.94*	-2.25
1.62	-10.2	11.96	-1.81	8.94	-2.18
4.37	-10.3	6.14	-1.75	8.94	-2.30
5.32	-10.6			4.47	-2.39
				4.47	-2.18
				4.47	-2.32

TABLE V

ENTHALPIES OF SOLUTION

Solvent: 15% DMSO

$(C_6H_5)_4PBr$		$NaB(C_6H_5)_4$		NaBr	
Wt. (mg)	ΔH_s	Wt. (mg)	ΔH_s	Wt. (mg)	ΔH_s
10.83*	3.90	12.60*	-1.34	38.04*	- .52
13.91	3.87	11.78	-1.26	18.33	- .51
14.48	4.05	10.98	-1.31	16.79	- .51
11.40	4.06	12.81	-1.40		

$(\underline{n}\text{-}C_4H_9)NCl$		$(\underline{n}\text{-}C_4H_9)_4NBr$		$(\underline{n}\text{-}C_4H_9)_4NI$	
Wt. (mg)	ΔH_s	Wt. (mg)	ΔH_s	Wt. (mg)	ΔH_s
16.16*	-5.39	12.03	- .25	36.30*	5.00
13.50	-5.25	29.11	- .27	23.82	5.15
12.52	-5.22	28.68	- .26	40.23	5.59
14.75	-5.26	23.65	- .27	31.23	5.67

TABLE V CONTINUED

ENTHALPIES OF SOLUTION

Solvent: 15% DMSO

NaOH		NaI		EtOAc	
Wt. (mg)	ΔH_s	Wt. (mg)	ΔH_s	Wt. (mg)	ΔH_s
2.98*	-10.3	23.32*	-2.33	8.94*	-1.12
3.01	-10.5	39.69	-2.34	8.94	-1.10
6.05	-10.6	25.14	-2.44	8.94	-1.12
		17.25	-2.31	8.94	-1.18

TABLE VI

ENTHALPIES OF SOLUTION

Solvent: 30% DMSO

$(C_6H_5)_4PBr$		$NaB(C_6H_5)_4$		NaBr	
Wt. (mg)	ΔH_s	Wt. (mg)	ΔH_s	Wt. (mg)	ΔH_s
6.48*	4.45	28.41*	.45	13.79*	- .74
13.98	4.60	25.29	.40	28.10	- .76
20.73	4.69	20.27*	.46	28.39*	- .74
16.66*	4.68	29.74	.51	22.82	- .74

TABLE VI CONTINUED

ENTHALPIES OF SOLUTION

Solvent: 30% DMSO

$(n\text{-}C_4H_9)_4NCl$		$(n\text{-}C_4H_9)_4NBr$		$(n\text{-}C_4H_9)_4NI$	
Wt. (mg)	ΔH_s	Wt. (mg)	ΔH_s	Wt. (mg)	ΔH_s
16.40*	-2.87	19.25*	1.99	19.90*	8.83
13.06	-2.72	32.51	1.92	14.34	8.63
13.96	-2.92	28.19	2.08	5.84*	8.54
14.57	-2.87	30.76	2.18	1.53	8.16
12.81	-2.87				

NaOH		NaI		EtOAc	
Wt. (mg)	ΔH_s	Wt. (mg)	ΔH_s	Wt. (mg)	ΔH_s
4.19*	-9.96	22.66*	-2.86	8.94*	.13
2.58	-10.9	27.88	-2.80	8.94	.27
1.94	-10.3	15.60	-2.90	8.94	.16

TABLE VII

ENTHALPIES OF SOLUTION

Solvent: 50% DMSO

$(C_6H_5)_4PBr$		$NaB(C_6H_5)_4$		NaBr	
Wt. (mg)	ΔH_s	Wt. (mg)	ΔH_s	Wt. (mg)	ΔH_s
2.67*	5.31	3.29*	-1.34	5.28*	-1.09
7.12	5.14	5.91	-1.38	9.75	-1.05
9.96	5.39	13.14	-1.28	21.17	-1.02
1.58	5.17			7.63*	-1.09
				8.06	-1.07
				11.16	-1.09
				20.87	-1.05

$(\underline{n}\text{-}C_4H_9)NCl$		$(\underline{n}\text{-}C_4H_9)NBr$		$(\underline{n}\text{-}C_4H_9)NI$	
Wt. (mg)	ΔH_s	Wt. (mg)	ΔH_s	Wt. (mg)	ΔH_s
4.11*	1.41	3.05*	5.88	3.08*	10.9
4.29	1.31	5.12	5.95	1.58	10.9
16.74	1.39	8.93	6.05	3.64	10.9
		17.85*	5.86	2.40	11.2

TABLE VII CONTINUED

ENTHALPIES OF SOLUTION

Solvent: 50% DMSO

NaOH		NaI		EtOAc	
Wt. (mg)	ΔH_s	Wt. (mg)	ΔH_s	Wt. (mg)	ΔH_s
3.72*	-7.30	18.02*	-3.70	8.94*	1.54
4.32	-7.39	25.25	-4.03	8.94	1.58
2.52	-7.23	10.27	-4.00	8.94	1.48
				8.94	1.72

$(\underline{n}\text{-}C_3H_7)OTs$	
Wt. (mg)	ΔH_s
4.67*	3.67
18.52	3.57
7.59	3.77
4.37	3.40
9.16	3.74

TABLE VIII

ENTHALPIES OF SOLUTION

Solvent: 60% DMSO

$(C_6H_5)_4PBr$		$NaB(C_6H_5)_4$		NaBr	
Wt. (mg)	ΔH_s	Wt. (mg)	ΔH_s	Wt. (mg)	ΔH_s
14.23*	4.74	7.88*	-4.14	7.48*	-1.62
6.29	4.71	7.15	-4.26	6.73	-1.53
15.00*	4.68	4.96	-4.22	12.47	-1.58
8.59*	4.57	18.58	-4.20	18.27	-1.62
3.51*	4.66			7.96	-1.48
5.55	4.73				
4.76*	4.52				
7.85	4.76				
13.39	4.81				
9.96*	4.57				
8.11	4.82				
5.21	4.56				

TABLE VIII CONTINUED

ENTHALPIES OF SOLUTION

Solvent: 60% DMSO

($\underline{n}$-C_4H_9)NCl		($\underline{n}$-C_4H_9)NBr		($\underline{n}$-C_4H_9)NI	
Wt. (mg)	ΔH_s	Wt. (mg)	ΔH_s	Wt. (mg)	ΔH_s
5.65*	3.02	13.84*	6.82	3.47*	13.3
8.49	3.08	5.64	6.68	4.25	13.5
14.17	3.04	5.26*	6.66	2.13	13.7
		4.62	6.82		
		13.03	6.85		
		7.02	6.99		
		11.73	6.70		

NaOH		NaI		EtOAc	
Wt. (mg)	ΔH_s	Wt. (mg)	ΔH_s	Wt. (mg)	ΔH_s
1.45*	-6.42	21.34*	-4.71	8.94*	2.13
1.35	-6.51	13.30	-4.91	8.94	2.01
0.64	-6.36	11.40	-5.00	8.94	1.85
				8.94	1.90

TABLE VIII CONTINUED

ENTHALPIES OF SOLUTION

Solvent: 60% DMSO

$(\underline{n}\text{-}C_3H_7)OTs$	
Wt. (mg)	ΔH_s
7.65*	3.63
2.70	3.42
4.57	3.58
18.50	3.58

TABLE IX

ENTHALPIES OF SOLUTION

Solvent: 65% DMSO

$(C_6H_5)_4PBr$		$NaB(C_6H_5)_4$		NaBr	
Wt. (mg)	ΔH_s	Wt. (mg)	ΔH_s	Wt. (mg)	ΔH_s
3.14*	3.58	3.63*	-6.26	6.72*	-1.90
5.18	3.82	8.03	-5.81	8.95	-2.05
10.95	3.68	13.16	-5.99	16.91	-1.81
		23.50	-6.08	11.32	-1.88
				6.51	-1.83

TABLE IX CONTINUED

ENTHALPIES OF SOLUTION

Solvent: 65% DMSO

($\underline{n}$-C_4H_9)NCl		($\underline{n}$-C_4H_9)NBr		($\underline{n}$-C_4H_9)NI	
Wt. (mg)	ΔH_s	Wt. (mg)	ΔH_s	Wt. (mg)	ΔH_s
3.81*	3.14	3.85*	7.00	4.99*	11.8
4.63	3.13	7.26	7.16	4.12	11.8
8.21	2.96	8.56	6.94	7.14	12.0
16.27	3.21	13.37	7.01	10.98	12.1
6.36	3.08				

NaOH		NaI		EtOAc	
Wt. (mg)	ΔH_s	Wt. (mg)	ΔH_s	Wt. (mg)	ΔH_s
1.08*	-5.86	4.84*	-5.39	8.94*	2.13
2.50	-5.71	9.89	-5.47	8.94	2.01
2.60	-5.66	13.30	-5.42	8.94	1.85
				8.94	1.90

TABLE IX CONTINUED

ENTHALPIES OF SOLUTION

Solvent: 65% DMSO

$(\underline{n}\text{-}C_3H_7)OTs$	
Wt. (mg)	ΔH_s
21.70*	3.14
1.67	2.97
5.77	2.92
10.90	3.08

TABLE X

ENTHALPIES OF SOLUTION

Solvent: 70% DMSO

$(C_6H_5)_4PBr$		$NaB(C_6H_5)_4$		NaBr	
Wt. (mg)	ΔH_s	Wt. (mg)	ΔH_s	Wt. (mg)	ΔH_s
3.98*	3.87	3.37*	-7.44	5.46*	-2.69
5.74	3.88	4.74	-7.59	3.56	-2.56
6.67	3.63	5.97	-7.43	11.48	-2.55
10.65	4.00	10.47	-7.63	11.81	-2.55
		6.96	-7.52	5.96	-2.46

TABLE X CONTINUED

ENTHALPIES OF SOLUTION

Solvent: 70% DMSO

$(n\text{-}C_4H_9)_4NCl$		$(n\text{-}C_4H_9)_4NBr$		$(n\text{-}C_4H_9)_4NI$	
Wt. (mg)	ΔH_s	Wt. (mg)	ΔH_s	Wt. (mg)	ΔH_s
4.21*	3.70	6.40*	7.52	1.68*	11.7
3.64	3.47	1.77*	7.00	8.04*	11.8
7.09	3.71	3.63*	7.39	5.87*	11.7
10.98	3.65	2.61*	7.35	16.04*	12.1
4.77	3.74	11.06*	7.31	7.24*	11.9
4.48*	3.63	16.58*	7.36		
		4.88*	7.17		
		13.43*	7.00		
		1.93*	7.22		

TABLE X CONTINUED

ENTHALPIES OF SOLUTION

Solvent: 70% DMSO

NaOH		NaI		EtOAc	
Wt. (mg)	ΔH_s	Wt. (mg)	ΔH_s	Wt. (mg)	ΔH_s
4.71*	-4.10	10.95*	-6.27	8.94*	1.86
3.27	-4.20	16.02	-5.85	8.94	1.82
5.80	-4.97	20.65	-6.09	8.94	1.72
		10.49	-6.11	8.94	1.84
		12.23	-6.23		

$(\underline{n}\text{-}C_3H_7)OTs$	
Wt. (mg)	ΔH_s
8.60*	3.13
2.48	3.18
5.59	3.14

TABLE XI

ENTHALPIES OF SOLUTION

Solvent: 80% DMSO

$(C_6H_5)_4PBr$		$NaB(C_6H_5)_4$		NaBr	
Wt. (mg)	ΔH_s	Wt. (mg)	ΔH_s	Wt. (mg)	ΔH_s
19.61*	2.42	3.88*	-10.6	6.20*	-3.54
7.11*	2.60	3.00*	-11.0	9.00*	-3.80
6.55*	2.61	5.92*	-11.1	15.36*	-3.73
5.39*	2.30	8.73*	-10.6	7.15*	-3.73
1.43*	2.48				

$(n\text{-}C_4H_9)_4NCl$		$(n\text{-}C_4H_9)_4NBr$		$(n\text{-}C_4H_9)_4NI$	
Wt. (mg)	ΔH_s	Wt. (mg)	ΔH_s	Wt. (mg)	ΔH_s
7.40*	4.14	5.41*	6.78	2.53*	11.5
10.84*	4.38	3.79*	6.90	1.74	10.8
17.16*	4.09	5.80*	6.78	16.11	11.4
2.78*	4.51	5.08*	6.52		
2.34*	4.62				

TABLE XI CONTINUED

ENTHALPIES OF SOLUTION

Solvent: 80% DMSO

NaOH		NaI		EtOAc	
Wt. (mg)	ΔH_s	Wt. (mg)	ΔH_s	Wt. (mg)	ΔH_s
3.54*	-3.52	6.51*	-8.04	8.94*	1.47
2.72	-3.38	10.80	-8.12	8.94	1.54
6.05	-3.43	9.57	-7.72	8.94	1.44
		11.49	-7.58	8.94	1.47
		4.09	-7.68		
		5.83	-7.86		

$(\underline{n}\text{-}C_3H_7)OTs$	
Wt. (mg)	ΔH_s
5.17*	2.66
6.88	2.52
4.33	2.59
21.57	2.70
2.70	2.57

TABLE XII

ENTHALPIES OF SOLUTION

Solvent: 85% DMSO

$(C_6H_5)_4PBr$		$NaB(C_6H_5)_4$		NaBr	
Wt. (mg)	ΔH_s	Wt. (mg)	ΔH_s	Wt. (mg)	ΔH_s
8.19*	2.21	7.44*	-12.3	9.03*	-4.12
8.31	1.91	4.38	-12.4	5.79	-4.20
9.67	2.13	7.35	-12.1	12.39	-4.45
7.45	1.88	4.50	-12.4	4.68	-4.47

NaOH	
Wt. (mg)	ΔH_s
9.94*	-2.81
6.72	-2.79
2.96	-2.70
5.04	-2.83

TABLE XIII

ENTHALPIES OF SOLUTION

Solvent: 90% DMSO

$(C_6H_5)_4PBr$		$NaB(C_6H_5)_4$		NaBr	
Wt. (mg)	ΔH_s	Wt. (mg)	ΔH_s	Wt. (mg)	ΔH_s
5.09*	1.66	6.02*	-13.2	4.87*	-4.89
4.11	1.65	6.42	-13.4	9.66	-5.10
11.90	1.55	4.12	-12.5	13.45	-4.56
9.21	1.70	6.70	-12.6	7.02	-4.98
		3.89	-13.3	4.98	-4.75

NaOH	
Wt. (mg)	ΔH_s
3.25*	-2.35
3.80	-2.10
4.84	-1.98

TABLE XIV

ENTHALPIES OF SOLUTION

Solvent: DMSO

$(C_6H_5)_4PBr$		$NaB(C_6H_5)_4$		NaBr	
Wt. (mg)	ΔH_s	Wt. (mg)	ΔH_s	Wt. (mg)	ΔH_s
30.96*	.26	5.41*	-14.0	3.29*	-6.28
22.85	.33	5.71	-14.4	4.38	-6.44
21.63	.42	9.75	-14.1	7.77	-6.23
23.73*	.42	11.28	-14.7	11.19	-6.00
19.21	.34				
15.06	.42				
31.23	.29				
6.34*	.24				
6.23	.22				
8.96	.22				
7.99	.43				

TABLE XIV CONTINUED

ENTHALPIES OF SOLUTION

Solvent: DMSO

$(n\text{-}C_4H_9)_4NCl$		$(n\text{-}C_4H_9)_4NBr$		$(n\text{-}C_4H_9)NI$	
Wt. (mg)	ΔH_s	Wt. (mg)	ΔH_s	Wt. (mg)	ΔH_s
4.93*	2.48	3.95*	4.32	2.80*	7.15
5.17*	2.41	2.48*	4.27	3.56*	7.30
5.27*	2.75	2.86*	4.32	3.96*	7.11
5.54*	2.58	10.69*	4.38	4.90*	7.13
7.29*	2.64	8.97*	4.43		
8.16*	2.51	3.53	4.38		
10.88*	2.59				

NaI		EtOAc		$(n\text{-}C_3H_7)OTs$	
Wt. (mg)	ΔH_s	Wt. (mg)	ΔH_s	Wt. (mg)	ΔH_s
4.64*	-11.8	8.94*	.54	16.09*	1.05
4.00	-11.3	8.94	.67	8.73	.96
2.33	-11.2	8.94	.59	5.29	.97
3.87	-11.8	8.94	.66	2.21	.96
		8.94	.63	5.35	.99

TABLE XIV CONTINUED

ENTHALPIES OF SOLUTION

Solvent: DMSO

$(\underline{n}\text{-}C_4H_9)_4Sn$		NaOH	
Wt. (mg)	ΔH_s	Wt. (mg)	ΔH_s
6.82*	3.80	2.36*	0.0
8.90	4.13	10.13	0.0
5.19	4.18	20.79	0.0
8.97	4.18		

TABLE XV

SUMMARY OF ENTHALPIES OF SOLUTION

% DMSO Salt	H_2O	15%	30%	50%	60%	65%
$(C_6H_5)_4PBr$	1.9 ±.1	4.0 ±.1	4.6 ±.1	5.2 ±.1	4.7 ±.1	3.7 ±.1
$NaB(C_6H_5)_4$	-4.5 ±.1	-1.3 ±.1	-0.46±.03	-1.3 ±.1	-4.2 ±.1	-6.0 ±.1
NaBr	-0.12±.01	-0.51±.03	-0.74±.01	-1. ±.1	-1.6 ±.1	-1.9 ±.1
$(n\text{-}C_4H_9)NCl$	-7.4 ±.1	-5.3 ±.1	-2.8 ±.1	1.4 ±.1	3.0 ±.1	3.1 ±.1
$(n\text{-}C_4H_9)NBr$	-2.0 ±.1	-0.27±.05	2.0 ±.1	5.9 ±.1	6.8 ±.1	7.0 ±.1
$(n\text{-}C_4H_9)NI$	4.0 ±.1	+5.3 ±.3	8.5 ±.2	11.0 ±.1	11.6 ±.1	11.9 ±.1
NaOH	-10.5 ±.2	-10.5 ±.1	-10.4 ±.3	-7.3 ±.1	-6.4 ±.1	-5.7 ±.1
NaI	-1.8 ±.1	-2.3 ±.1	-2.8 ±.10	-3.9 ±.1	-4.9 ±.1	-5.4 ±.1
EtOAc	-2.3 ±.1	-1.1 ±.1	0.19±.06	1.6 ±.1	1.9 ±.1	2.0 ±.1
$n\text{-}C_3H_7$ OTs				3.7 ±.1	3.5 ±.1	3.0 ±.1

TABLE XV CONTINUED

SUMMARY OF ENTHALPIES OF SOLUTION

% DMSO Salt	70%	80%	85%	90%	DMSO
$(C_6H_5)_4PBr$	3.8 ±.1	2.5 ±.1	2.0 ±.1	1.6 ±.1	.34±.07
$NaB(C_6H_5)_4$	-7.5 ±.1	-10.8 ±.2	-12.3 ±.1	-13.0 ±.4	-14.3 ±.1
NaBr	-2.6 ±.1	-3.7 ±.1	-4.3 ±.1	-4.9 ±.2	-6.2 ±.1
$(n\text{-}C_4H_9)_4NCl$	3.6 ±.1	4.3 ±.2			2.6 ±.1
$(n\text{-}C_4H_9)_4NBr$	7.3 ±.3	6.7 ±.1			4.3 ±.1
$(n\text{-}C_4H_9)_4NI$	11.9 ±.1	11.2 ±.3			7.2 ±.1
NaOH	-4.1 ±.1	-3.4 ±.1	-2.8 ±.1	-2.1 ±.1	0.0
NaI	-6.1 ±.1	-7.8 ±.2			-11.5 ±.3
EtOAc	1.8 ±.1	1.5 ±.1			0.62±.04
$(n\text{-}C_3H_7)OTs$	3.1 ±.1	2.6 ±.1			0.99±.03
$(n\text{-}C_4H_9)Sn$					4.1 ±.1

TABLE XVI

CALCULATION OF ENTHALPIES OF TRANSFER OF SALTS FROM WATER TO 15% DMSO

Salt	$\Delta H_{s\ H_2O}$	$\Delta H_{s\ 15\%\ DMSO}$	$\Delta\Delta H_s$
$(C_6H_5)_4PBr$	1.9	4.0	2.1
$NaB(C_6H_5)_4$	-4.5	-1.3	3.2
NaBr	-0.12	-0.51	-.39
$(\underline{n}\text{-}C_4H_9)_4NCl$	-7.4	-5.3	2.1
$(\underline{n}\text{-}C_4H_9)_4NBr$	-2.0	- .27	1.7
$(\underline{n}\text{-}C_4H_9)_4NI$	4.0	5.3	1.3
NaOH	-10.5	-10.5	0
EtOAc	-2.3	-1.1	1.2
NaI	-1.8	-2.3	- .5

TABLE XVII

CALCULATION OF ENTHALPIES OF TRANSFER OF SALTS FROM WATER TO 30% DMSO

Salt	ΔH_s H_2O	ΔH_s 30% DMSO	$\Delta\Delta H_s$
$(C_6H_5)_4PBr$	1.9	4.6	2.7
$NaB(C_6H_5)_4$	-4.5	0.46	5.0
NaBr	-0.2	-0.74	-0.62
$(n\text{-}C_4H_9)_4NCl$	-7.4	-2.8	4.6
$(n\text{-}C_4H_9)_4NBr$	-2.0	2.0	4.0
$(n\text{-}C_4H_9)_4NI$	4.0	8.5	4.5
NaOH	-10.5	-10.4	0.1
EtOAc	-2.3	0.19	2.5
NaI	-1.8	-2.8	-1.0

TABLE XVIII

CALCULATION OF ENTHALPIES OF TRANSFER OF SALTS FROM WATER TO 50% DMSO

Salt	ΔH_s H_2O	ΔH_s 50% DMSO	$\Delta\Delta H_s$
$(C_6H_5)_4PBr$	1.9	5.2	3.3
$NaB(C_6H_5)_4$	-4.5	-1.3	3.2
NaBr	-0.12	-1.0	- .95
$(\underline{n}\text{-}C_4H_9)_4NCl$	-7.4	1.4	8.8
$(\underline{n}\text{-}C_4H_9)_4NBr$	-2.0	5.9	7.9
$(\underline{n}\text{-}C_4H_9)_4NI$	4.0	11.0	7.0
NaOH	-10.5	-7.3	3.2
EtOAc	-2.3	1.6	3.9
NaI	-1.8	-3.9	-2.1

TABLE XIX

CALCULATION OF ENTHALPIES OF TRANSFER OF SALTS FROM WATER TO 60% DMSO

Salt	ΔH_s H_2O	ΔH_s 60% DMSO	$\Delta\Delta H_s$
$(C_6H_5)_4PBr$	1.9	4.7	2.8
$NaB(C_6H_5)_4$	-4.5	-4.2	.3
NaBr	-0.12	-1.6	-1.5
$(\underline{n}\text{-}C_4H_9)_4NCl$	-7.4	3.0	10.4
$(\underline{n}\text{-}C_4H_9)_4NBr$	-2.0	6.8	8.8
$(\underline{n}\text{-}C_4H_9)_4NI$	4.0	11.6	7.6
NaOH	-10.5	-6.4	4.1
EtOAc	-2.3	1.9	4.2
NaI	-1.8	-4.9	-3.1

TABLE XX

CALCULATION OF ENTHALPIES OF TRANSFER OF SALTS FROM WATER TO 65% DMSO

Salt	ΔH_s H_2O	ΔH_s 65% DMSO	$\Delta\Delta H_s$
$(C_6H_5)_4PBr$	1.9	3.7	1.8
$NaB(C_6H_5)_4$	-4.5	-6.0	-1.5
NaBr	-0.12	-1.9	-1.8
$(\underline{n}\text{-}C_4H_9)_4NCl$	-7.4	3.1	10.5
$(\underline{n}\text{-}C_4H_9)_4NBr$	-2.0	7.0	9.0
$(\underline{n}\text{-}C_4H_9)_4NI$	4.0	11.9	7.9
NaOH	-10.5	-5.7	4.8
EtOAc	-2.3	2.0	4.3
NaI	-1.8	-5.4	-3.6

TABLE XXI

CALCULATION OF ENTHALPIES OF TRANSFER OF SALTS FROM WATER TO 70% DMSO

Salt	ΔH_s H_2O	ΔH_s 70% DMSO	$\Delta\Delta H_s$
$(C_6H_5)_4PBr$	1.9	3.8	1.9
$NaB(C_6H_5)_4$	-4.5	-7.5	-3.0
NaBr	-0.12	-2.6	-2.5
$(\underline{n}\text{-}C_4H_9)_4NCl$	-7.4	3.6	11.0
$(\underline{n}\text{-}C_4H_9)_4NBr$	-2.0	7.3	9.3
$(\underline{n}\text{-}C_4H_9)_4NI$	4.0	11.9	7.9
NaOH	-10.5	-4.1	6.4
EtOAc	-2.3	1.8	4.1
NaI	-1.8	-6.1	-4.3

TABLE XXII

CALCULATION OF ENTHALPIES OF TRANSFER OF SALTS FROM WATER TO 80% DMSO

Salt	ΔH_s H_2O	ΔH_s 80% DMSO	$\Delta\Delta H_s$
$(C_6H_5)_4PBr$	1.9	2.5	.6
$NaB(C_6H_5)_4$	-4.5	-10.8	-6.3
NaBr	-0.12	-3.7	-3.6
$(\underline{n}\text{-}C_4H_9)_4NCl$	-7.4	4.3	11.7
$(\underline{n}\text{-}C_4H_9)_4NBr$	-2.0	6.7	8.7
$(\underline{n}\text{-}C_4H_9)_4NI$	4.0	11.2	7.2
NaOH	-10.5	-3.4	7.1
EtOAc	-2.3	1.5	3.8
NaI	-1.8	-7.8	-6.0

TABLE XXIII

CALCULATION OF ENTHALPIES OF TRANSFER OF SALTS FROM WATER TO 85% DMSO

Salt	ΔH_s H_2O	ΔH_s 85% DMSO	$\Delta\Delta H_s$
$(C_6H_5)_4PBr$	1.9	2.0	.1
$NaB(C_6H_5)_4$	-4.5	-12.3	-7.8
NaBr	-0.12	-4.3	-4.2
NaOH	-10.5	-2.9	7.7

TABLE XXIV

CALCULATION OF ENTHALPIES OF TRANSFER OF SALTS FROM WATER TO 90% DMSO

Salt	ΔH_s H_2O	ΔH_s 90% DMSO	$\Delta\Delta H_s$
$(C_6H_5)_4PBr$	1.9	1.6	- .3
$NaB(C_6H_5)_4$	-4.5	-13.0	-8.5
NaBr	-0.12	-4.9	-4.8
NaOH	-10.5	-2.1	8.4

TABLE XXV

CALCULATION OF ENTHALPIES OF TRANSFER OF SALTS FROM WATER TO 100% DMSO

Salt	ΔH_s H_2O	ΔH_s 100% DMSO	$\Delta\Delta H_s$
$(C_6H_5)_4PBr$	1.9	0.34	1.6
$NaB(C_6H_5)_4$	-4.5	-14.3	-9.8
NaBr	-0.12	-6.2	-6.1
$(\underline{n}\text{-}C_4H_9)_4NCl$	-7.4	2.6	10.0
$(\underline{n}\text{-}C_4H_9)_4NBr$	-2.0	4.3	6.3
$(\underline{n}\text{-}C_4H_9)_4NI$	4.0	7.2	3.2
NaOH	-10.5	0.0	10.5
EtOAc	-2.3	.62	2.9
NaI	-1.8	-11.5	-9.7

TABLE XXVI

CALCULATION OF SINGLE ION ENTHALPIES OF TRANSFER OF TETRAPHENYLPHOSPHONIUM AND TETRABUTYLBORATE IONS FROM WATER TO AQUEOUS DMSO

% DMSO	1/2	$[\Delta\Delta H_s$	$(C_6H_5)_4PBr$	+	$\Delta\Delta H$ $NaB(C_6H_5)_4$	-	$\Delta\Delta H$ NaBr]	=	$\Delta\Delta H$ $(C_6H_5)_4P^+$	=	$\Delta\Delta H$ $^-B(C_6H_5)_4$
15	1/2	(+2.1		+	3.2		+0.3)	=	2.8		
30	1/2	(+2.7		+	5.0		+0.6)	=	4.1		
50	1/2	(+3.3		+	3.2		+0.9)	=	3.7		
60	1/2	(+2.8		+	0.3		+1.5)	=	2.3		
65	1/2	(+1.8		-	1.5		+1.8)	=	1.0		
70	1/2	(+1.9		-	3.0		+2.5)	=	0.7		
80	1/2	(+0.6		-	6.3		+3.6)	=	-1.0		
85	1/2	(+0.1		-	7.8		+4.2)	=	-1.7		
90	1/2	(-0.3		-	8.5		+4.8)	=	-2.0		
DMSO	1/2	(-1.6		-	9.8		+6.1)	=	-2.6		

TABLE XXVII

CALCULATION OF SINGLE ION ENTHALPIES OF TRANSFER OF BROMIDE ION FROM WATER TO AQUEOUS DMSO

% DMSO	$\Delta\Delta H_s$ $(C_6H_5)_4PBr$	-	$\Delta\Delta H_s$ $(C_6H_5)_4P^+$	=	$\Delta\Delta H_s$ Br^-
15	2.1	-	2.8	=	-0.7
30	2.7	-	4.1	=	-1.4
50	3.2	-	3.7	=	-0.5
60	2.8	-	2.3	=	0.5
65	1.8	-	1.0	=	0.8
70	1.9	-	0.7	=	1.2
80	0.6	+	1.0	=	1.6
85	0.1	+	1.7	=	1.8
90	-0.3	+	2.0	=	1.7
DMSO	-1.6	+	2.6	=	1.0

TABLE XXVIII

CALCULATION OF SINGLE ION ENTHALPIES OF TRANSFER OF SODIUM ION FROM WATER TO AQUEOUS DMSO

% DMSO	$\Delta\Delta H_s$ $NaB(C_6H_5)_4$	-	$\Delta\Delta H_s$ $^-B(C_6H_5)_4$	=	$\Delta\Delta H_s$ Na^+
15	3.2	-	2.8	=	0.4
30	5.0	-	4.1	=	0.9
50	3.2	-	3.7	=	-0.5
60	0.3	-	2.3	=	-2.0
65	-1.5	-	1.0	=	-2.5
70	-3.0	-	0.7	=	-3.7
80	-6.3	+	1.0	=	-5.3
85	-7.8	+	1.7	=	-6.1
90	-8.5	+	2.0	=	-6.5
DMSO	-9.8	+	2.6	=	-7.2

TABLE XXIX

CALCULATION OF SINGLE ION ENTHALPIES OF TRANSFER OF TETRABUTYLAMMONIUM ION FROM WATER TO AQUEOUS DMSO

% DMSO	$\Delta\Delta H_s$ $(n\text{-}C_4H_9)_4NBr$	-	$\Delta\Delta H_s$ Br^-	=	$\Delta\Delta H_s$ $(n\text{-}C_4H_9)_N^+$
15	1.7	+	.7	=	2.4
30	4.0	+	1.4	=	5.4
50	7.9	+	0.5	=	8.4
60	8.8	-	0.5	=	8.3
65	9.0	-	0.8	=	8.2
70	9.3	-	1.2	=	8.1
80	8.7	-	1.6	=	7.1
DMSO	6.3	-	1.0	=	5.3

TABLE XXX

CALCULATION OF SINGLE ION ENTHALPIES OF TRANSFER OF CHLORIDE ION FROM WATER TO AQUEOUS DMSO

% DMSO	$\Delta\Delta H_s$ $(\underline{n}\text{-}C_4H_9)_4NCl$	-	$\Delta\Delta H_s$ $(\underline{n}\text{-}C_4H_9)_4N^+$	=	$\Delta\Delta H_s$ Cl^-
15	2.1	-	2.4	=	-0.3
30	4.6	-	5.4	=	-0.8
50	8.8	-	8.4	=	0.4
60	10.4	-	8.3	=	2.1
65	10.5	-	8.2	=	2.3
70	11.0	-	8.1	=	2.9
80	11.7	-	7.1	=	4.6
DMSO	10.0	-	5.3	=	4.7

TABLE XXXI

CALCULATION OF SINGLE ION ENTHALPIES OF TRANSFER OF IODIDE ION FROM WATER TO AQUEOUS DMSO

% DMSO	$\Delta\Delta H_s$ NaI	-	$\Delta\Delta H_s$ Na^+	=	I^-
15	-0.57	-	0.4	=	-0.97
30	-1.0	-	0.9	=	-1.9
50	-2.1	+	0.5	=	-1.6
60	-3.1	+	2.0	=	-1.1
65	-3.6	+	2.5	=	-1.1
70	-4.3	+	3.7	=	-0.6
80	-6.0	+	5.3	=	-0.7
DMSO	-9.7	+	7.2	=	-2.5

TABLE XXXII

CALCULATION OF SINGLE ION ENTHALPIES OF TRANSFER OF HYDROXIDE ION FROM WATER TO AQUEOUS DMSO

% DMSO	$\Delta\Delta H_s$ NaOH	-	$\Delta\Delta H$ Na^+	=	$\Delta\Delta H$ ^-OH
15	0.0	-	0.4	=	-0.4
30	0.1	-	0.9	=	-0.8
50	3.2	+	0.5	=	3.7
60	4.1	+	2.0	=	6.1
65	4.8	+	2.5	=	7.3
70	6.4	+	3.7	=	10.1
80	7.1	+	5.3	=	12.4
85	7.7	+	6.1	=	13.8
90	8.4	+	6.5	=	14.9
DMSO	10.5	+	7.2	=	17.7

TABLE XXXIII

SUMMARY OF SINGLE ION ENTHALPIES OF TRANSFER FROM WATER TO AQUEOUS DMSO AT 25°

% DMSO	Ion $(C_6H_5)_4P^+ = {}^-B(C_6H_5)_4$	$(n\text{-}C_4H_9)_4N^+$	Na^+	^-OH	Cl^-	Br^-	I^-
15	2.8	2.4	0.4	-0.4	-0.3	-0.7	-0.97
30	4.1	5.4	0.9	-0.8	-0.8	-1.4	-1.9
50	3.7	8.4	-0.5	3.7	0.4	-0.5	-1.6
60	2.3	8.3	-2.0	6.1	2.1	0.5	-1.1
65	1.0	8.2	-2.5	7.3	2.3	0.8	-1.1
70	0.7	8.1	-3.7	10.1	2.9	1.2	-0.6
80	-1.0	7.1	-5.3	12.4	4.6	1.6	-0.7
85	-1.7	--	-6.1	13.8	--	1.8	--
90	-2.0	--	-6.5	14.9	--	1.7	--
DMSO	-2.6	5.3	-7.2	17.7	4.7	1.0	-2.5

V

DISCUSSION

DISCUSSION

A. ENTHALPIES OF SOLUTION

Enthalpies of solution are presented in Tables IV-XIV and summarized in Table XV. Since an actual error determination cannot be made, the values are listed with the average deviation. Propyl tosylate was not soluble in solvent mixtures containing less than 50% by volume DMSO. Tetra-n-butyltin was soluble only in DMSO. Table XXXIV compares some enthalpies of solution obtained in this study with values previously reported in the literature. This problem is especially pronounced in highly aqueous solutions. Since we have noticed that tetra-n-butylammonium iodide has a tendency to float on the solvent instead of dissolving, some of our values for the heat of solution of this salt could quite possibly be in error. The enthalpy of solution of sodium iodide was measured to check for these errors.

Our value for the heat of solution of tetra-n-butyl ammonium chloride in DMSO is lower (1.2 and 0.7 kcal $mole^{-1}$) than the two values reported in the literature [22,50]. The value for the enthalpy of solution of tetra-n-butylammonium bromide is about 0.7 kcal $mole^{-1}$ lower than the literature values [22,50]. The enthalpy of solution of tetra-n-butyl

TABLE XXXIV

COMPARISON OF ENTHALPIES OF SOLUTION AT 25°

Solvent / Salt	H_2O	DMSO	80% DMSO
$NaB(C_6H_5)_4$	-4.5[a]	-14.3[a]	
	-4.77[b]	-14.2[d]	
	-5.2[c]	-14.2[f]	
$(n\text{-}C_4H_9)_4NCl$	-7.4[a]	2.6[a]	4.35[a]
	-7.3[d]	3.7[d]	4.4[g]
	-7.14[i]	3.22[i]	
$(n\text{-}C_4H_9)_4NBr$	-2.0[a]	4.3[a]	6.7[a]
	-2.2[d]	5.1[d]	7.1[g]
	-2.0[i]	4.95[i]	
$(n\text{-}C_4H_9)_4NI$	4.0[a]	7.2[a]	11.2[a]
	3.8[d]	7.2[d]	8.3[g]
		7.27[i]	
NaBr	-0.12[a]		
	-0.14[h]		
NaI	-1.8[a]	--	
	-1.9[e]	--	
	-1.80[h]	--	

[a]This study. [b]Ref. 47. [c]Ref. 48. [d]Ref. 22. [e]National Standards Reference Data System NRSDS-NBS 2. [f]Ref. 4. [g]Ref. 45. [h]Ref. 49. [i]Ref. 50

ammonium iodide in 80% by volume DMSO is approximately 3 kcal mole^{-1} higher than the value reported by Fuchs and Plumlee [45].

None of the salts showed a concentration dependence in any of the solvent combinations. The solvolysis of n-propyl tosylate in aqueous DMSO is slow enough that it does not interfere with the enthalpy measurements [51].

In Figures 1-9 the enthalpy of solution is plotted versus the volume percent of added DMSO.

B. SINGLE ION ENTHALPIES OF TRANSFER

The single ion enthalpies of transfer are based on the assumption that the enthalpy of transfer of tetraphenylphosphonium ion is equal to the enthalpy of transfer of the tetraphenylborate ion. Since Grunwald and coworkers [7] first proposed this assumption, it has been extensively used [5,7]. Dividing the enthalpy of transfer of tetraphenylphosphonium tetraphenylborate salt by one-half gives the enthalpy of transfer value for the individual ions. The enthalpy of transfer for the tetraphenylphosphonium tetraphenylborate salt is taken as the sum of the enthalpies of transfer for tetraphenylphosphonium bromide and sodium tetraphenylborate, minus the enthalpy of transfer for sodium bromide. The enthalpy of transfer for bromide ion is the enthalpy of transfer for tetraphenylphosphonium bromide minus the value for tetra-

FIGURE 1

PLOT OF ENTHALPY OF SOLUTION VERSUS DMSO CONCENTRATION FOR TETRAPHENYLPHOSPHONIUM BROMIDE

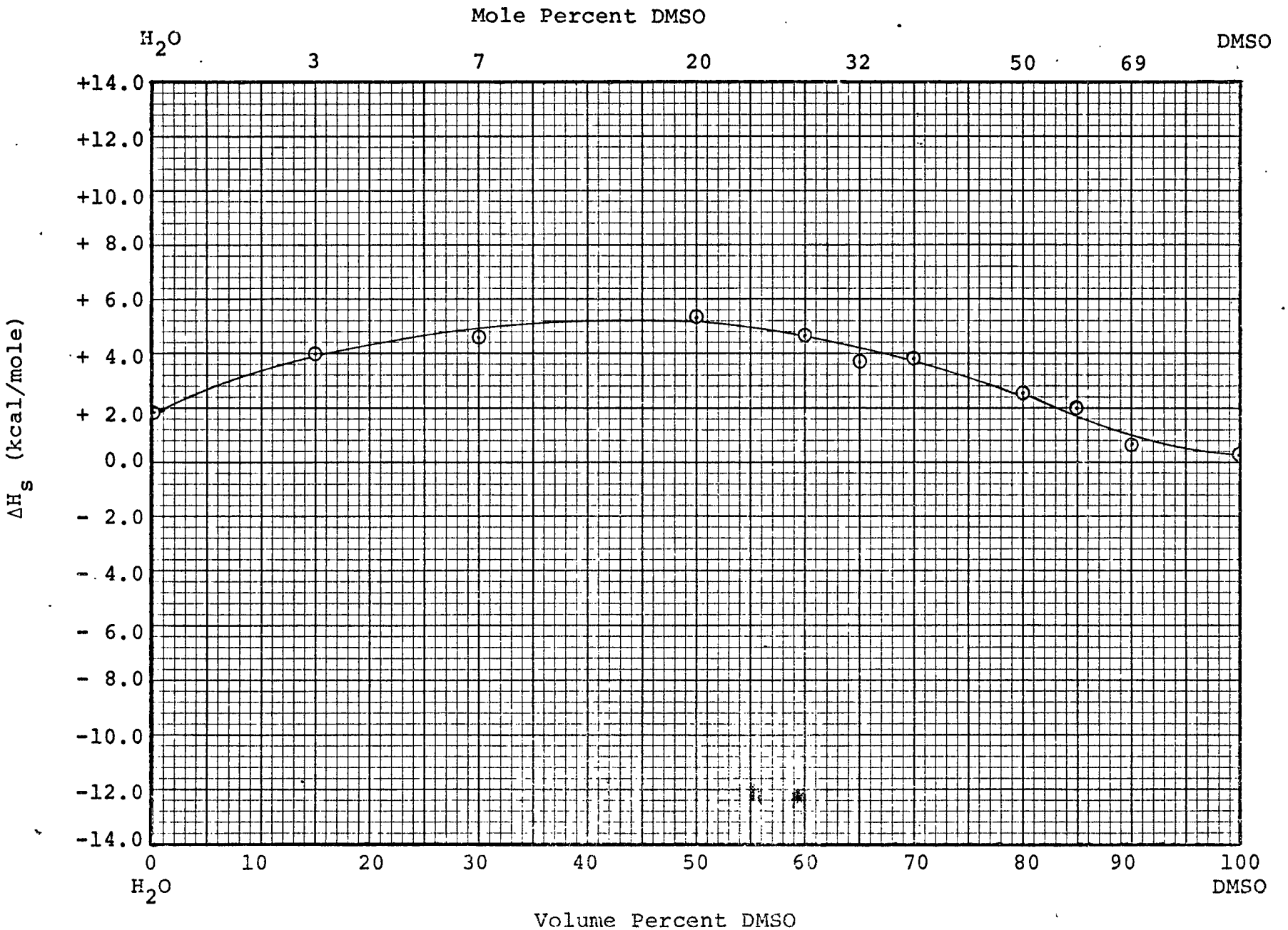

Mole Percent DMSO
H_2O
DMSO
3
7
20
32
50
69
+14.0
+12.0
+10.0
+ 8.0
+ 6.0
+ 4.0
+ 2.0
0.0
- 2.0
- 4.0
- 6.0
- 8.0
-10.0
-12.0
-14.0
ΔH_s (kcal/mole)
0
10
20
30
40
50
60
70
80
90
100
H_2O
DMSO
Volume Percent DMSO

FIGURE 2

PLOT OF ENTHALPY OF SOLUTION VERSUS DMSO CONCENTRATION FOR SODIUM TETRAPHENYLBORATE

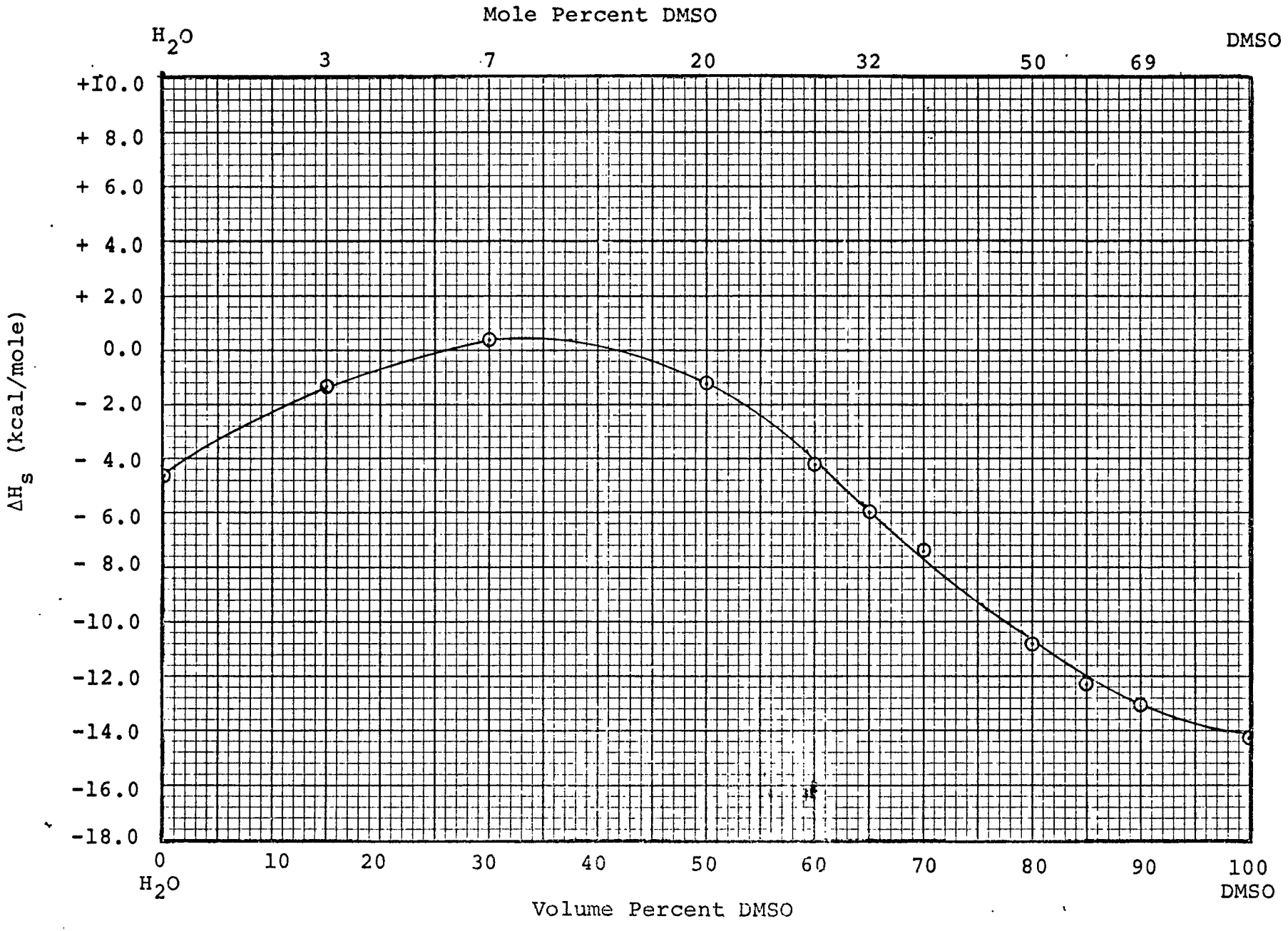

Mole Percent DMSO
H_2O
DMSO
3
7
20
32
50
69
+10.0
+ 8.0
+ 6.0
+ 4.0
+ 2.0
0.0
- 2.0
- 4.0
- 6.0
- 8.0
-10.0
-12.0
-14.0
-16.0
-18.0
ΔH_s (kcal/mole)
0
10
20
30
40
50
60
70
80
90
100
H_2O
DMSO
Volume Percent DMSO

FIGURE 3

PLOT OF ENTHALPY OF SOLUTION VERSUS DMSO CONCENTRATION FOR SODIUM BROMIDE

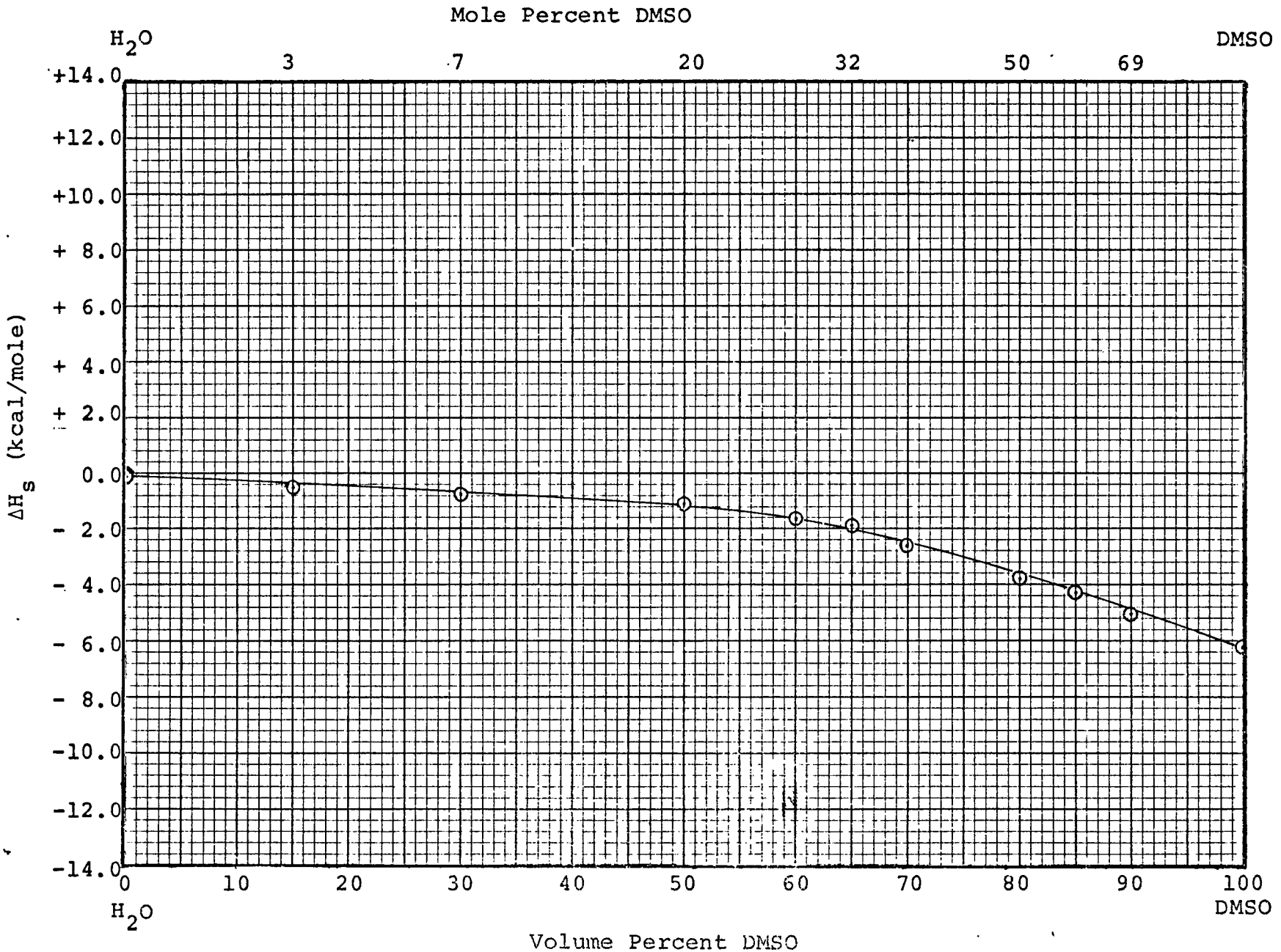

Mole Percent DMSO
H2O
DMSO
3
7
20
32
50
69
+14.0
+12.0
+10.0
+ 8.0
+ 6.0
+ 4.0
+ 2.0
0.0
- 2.0
- 4.0
- 6.0
- 8.0
-10.0
-12.0
-14.0
ΔHs (kcal/mole)
0
10
20
30
40
50
60
70
80
90
100
H2O
DMSO
Volume Percent DMSO

FIGURE 4

PLOT OF ENTHALPY OF SOLUTION VERSUS DMSO CONCENTRATION FOR TETRA-n-BUTYLAMMONIUM CHLORIDE

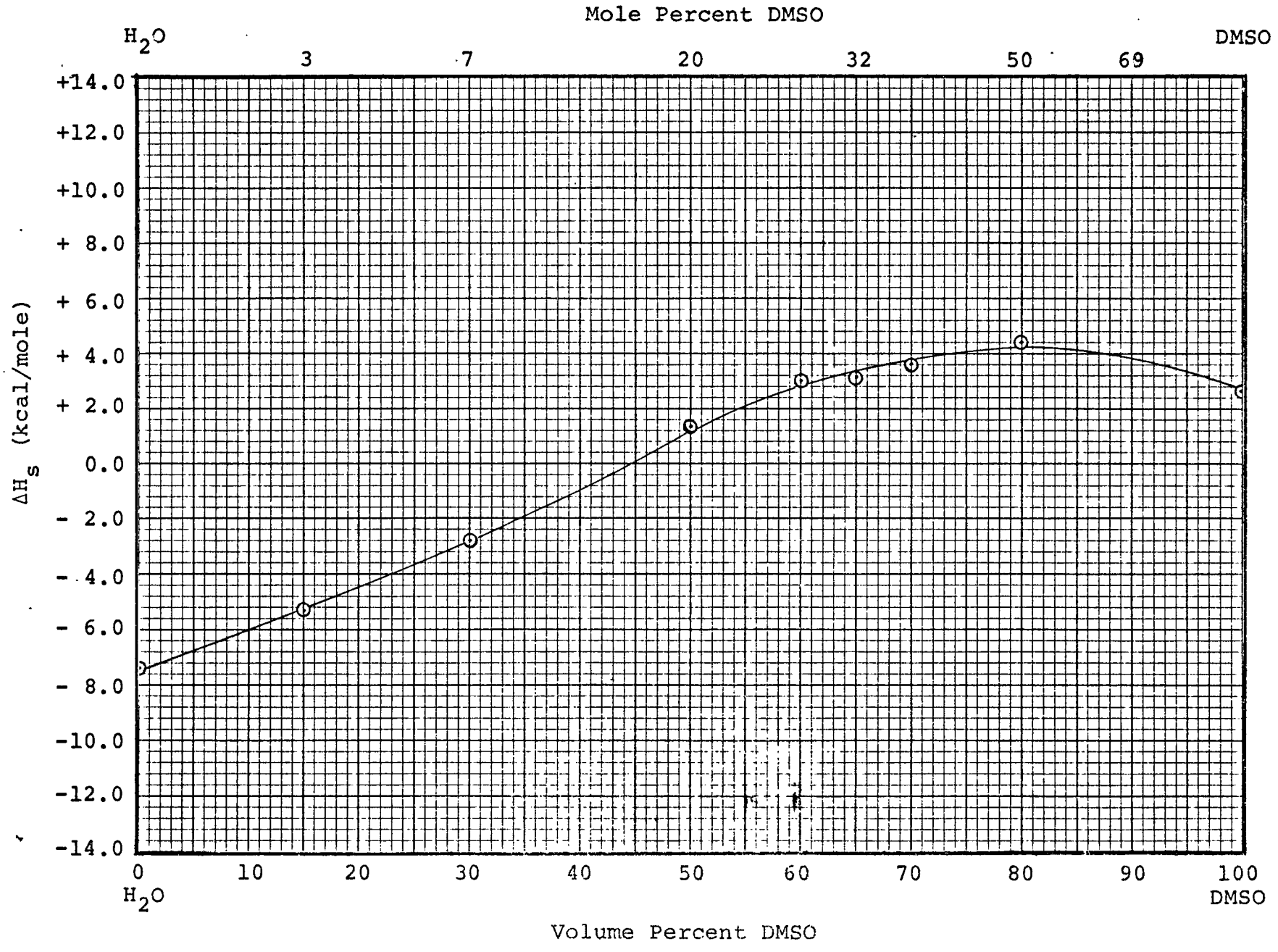

Mole Percent DMSO
H_2O
DMSO
3
7
20
32
50
69
+14.0
+12.0
+10.0
+ 8.0
+ 6.0
+ 4.0
+ 2.0
0.0
- 2.0
- 4.0
- 6.0
- 8.0
-10.0
-12.0
-14.0
ΔH_s (kcal/mole)
0
10
20
30
40
50
60
70
80
90
100
H_2O
DMSO
Volume Percent DMSO

FIGURE 5

PLOT OF ENTHALPY OF SOLUTION VERSUS DMSO CONCENTRATION FOR TETRA-n-BUTYLAMMONIUM BROMIDE

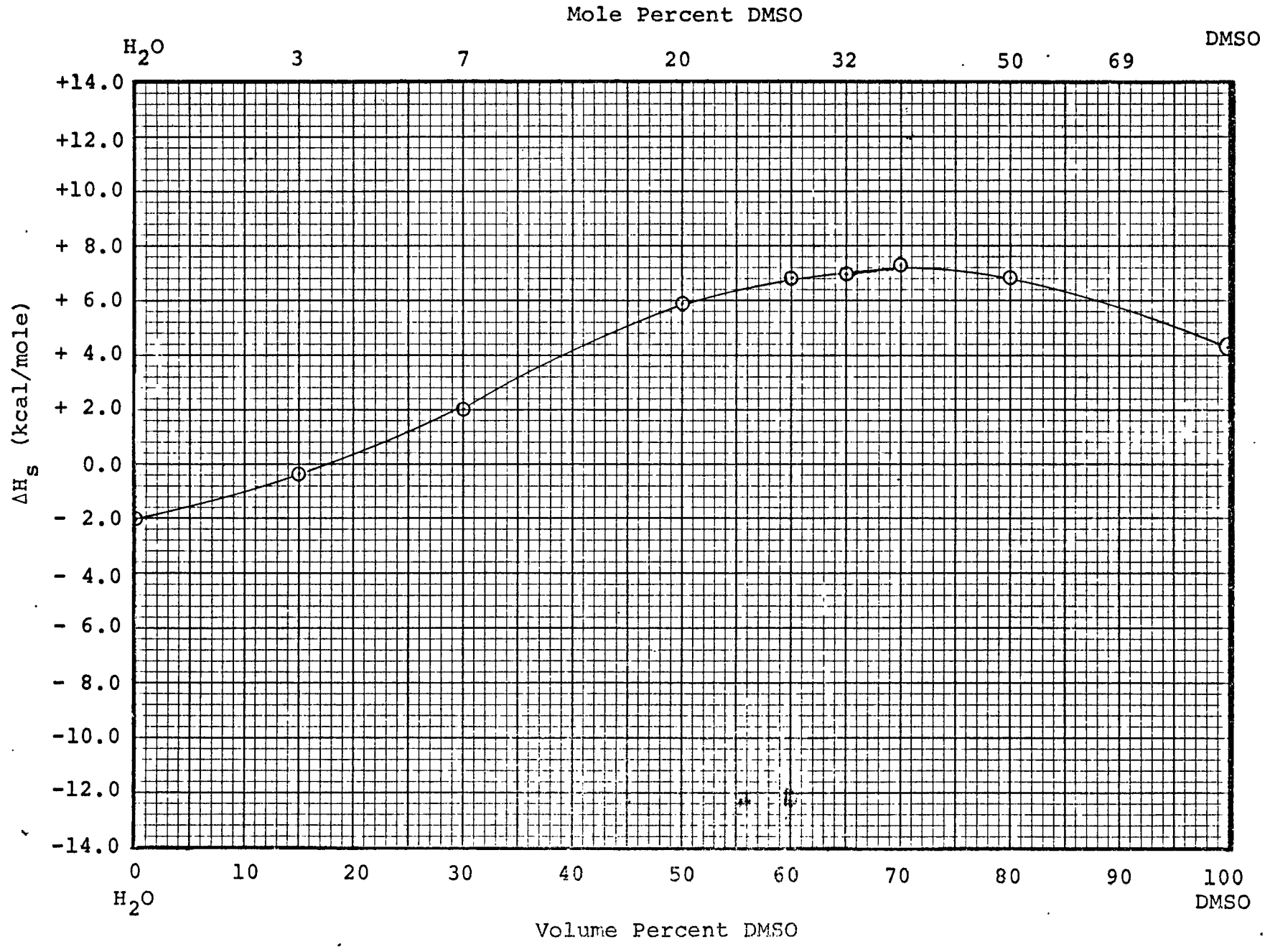

Mole Percent DMSO
H2O
3
7
20
32
50
69
DMSO
+14.0
+12.0
+10.0
+ 8.0
+ 6.0
+ 4.0
+ 2.0
0.0
- 2.0
- 4.0
- 6.0
- 8.0
-10.0
-12.0
-14.0
ΔHs (kcal/mole)
0
10
20
30
40
50
60
70
80
90
100
H2O
DMSO
Volume Percent DMSO

FIGURE 6

PLOT OF ENTHALPY OF SOLUTION VERSUS DMSO CONCENTRATION FOR TETRA-n-BUTYLAMMONIUM ICDIDE

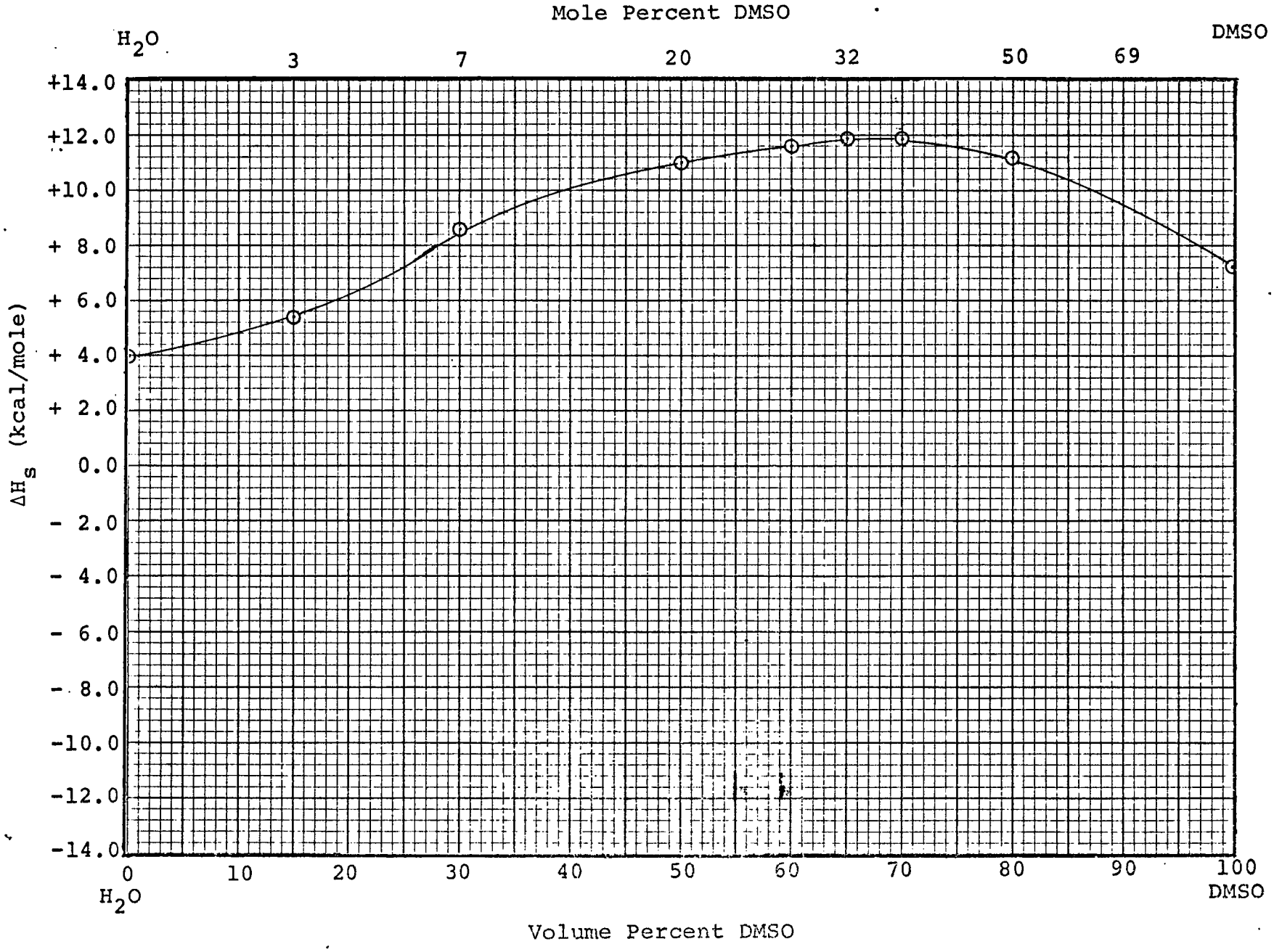

Mole Percent DMSO
H_2O
DMSO
3
7
20
32
50
69
+14.0
+12.0
+10.0
+ 8.0
+ 6.0
+ 4.0
+ 2.0
0.0
- 2.0
- 4.0
- 6.0
- 8.0
-10.0
-12.0
-14.0
ΔH_s (kcal/mole)
0
10
20
30
40
50
60
70
80
90
100
H_2O
DMSO
Volume Percent DMSO

FIGURE 7

PLOT OF ENTHALPY OF SOLUTION VERSUS DMSO CONCENTRATION FOR SODIUM IODIDE

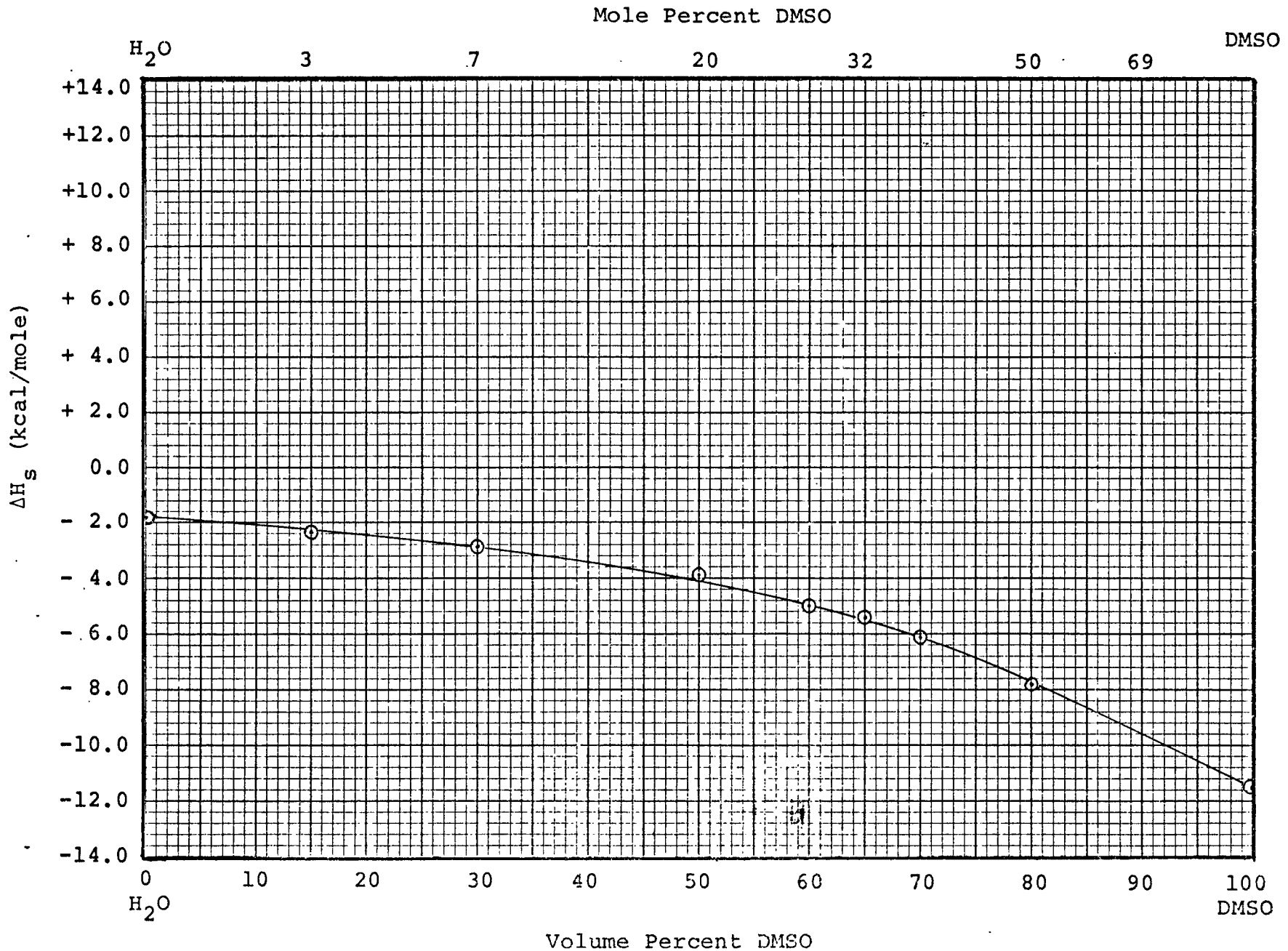

Mole Percent DMSO
H2O
DMSO
3
7
20
32
50
69
+14.0
+12.0
+10.0
+ 8.0
+ 6.0
+ 4.0
+ 2.0
0.0
- 2.0
- 4.0
- 6.0
- 8.0
-10.0
-12.0
-14.0
ΔHs (kcal/mole)
0
10
20
30
40
50
60
70
80
90
100
H2O
DMSO
Volume Percent DMSO

FIGURE 8

PLOT OF ENTHALPY OF SOLUTION VERSUS DMSO CONCENTRATION FOR SODIUM HYDROXIDE

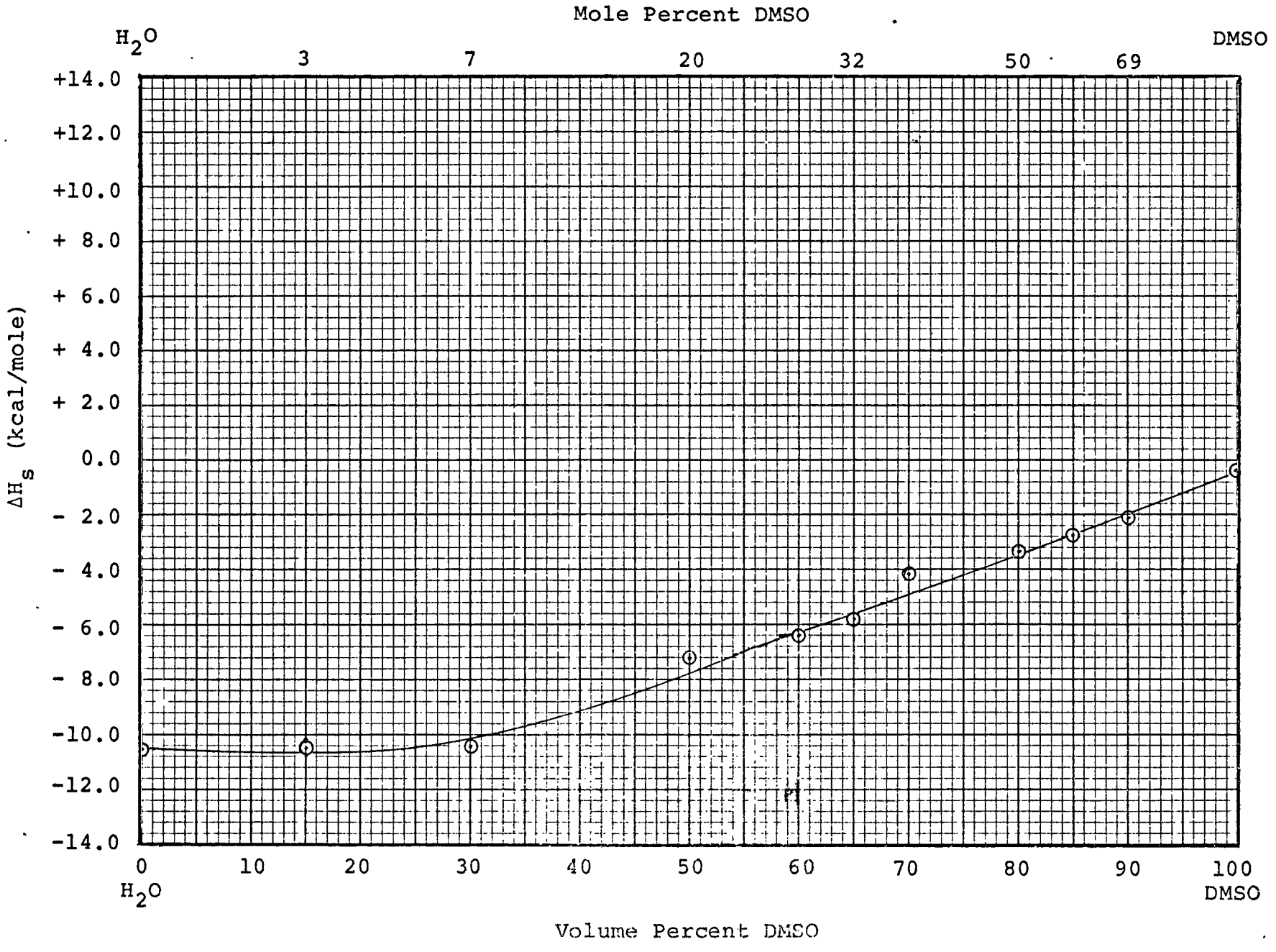
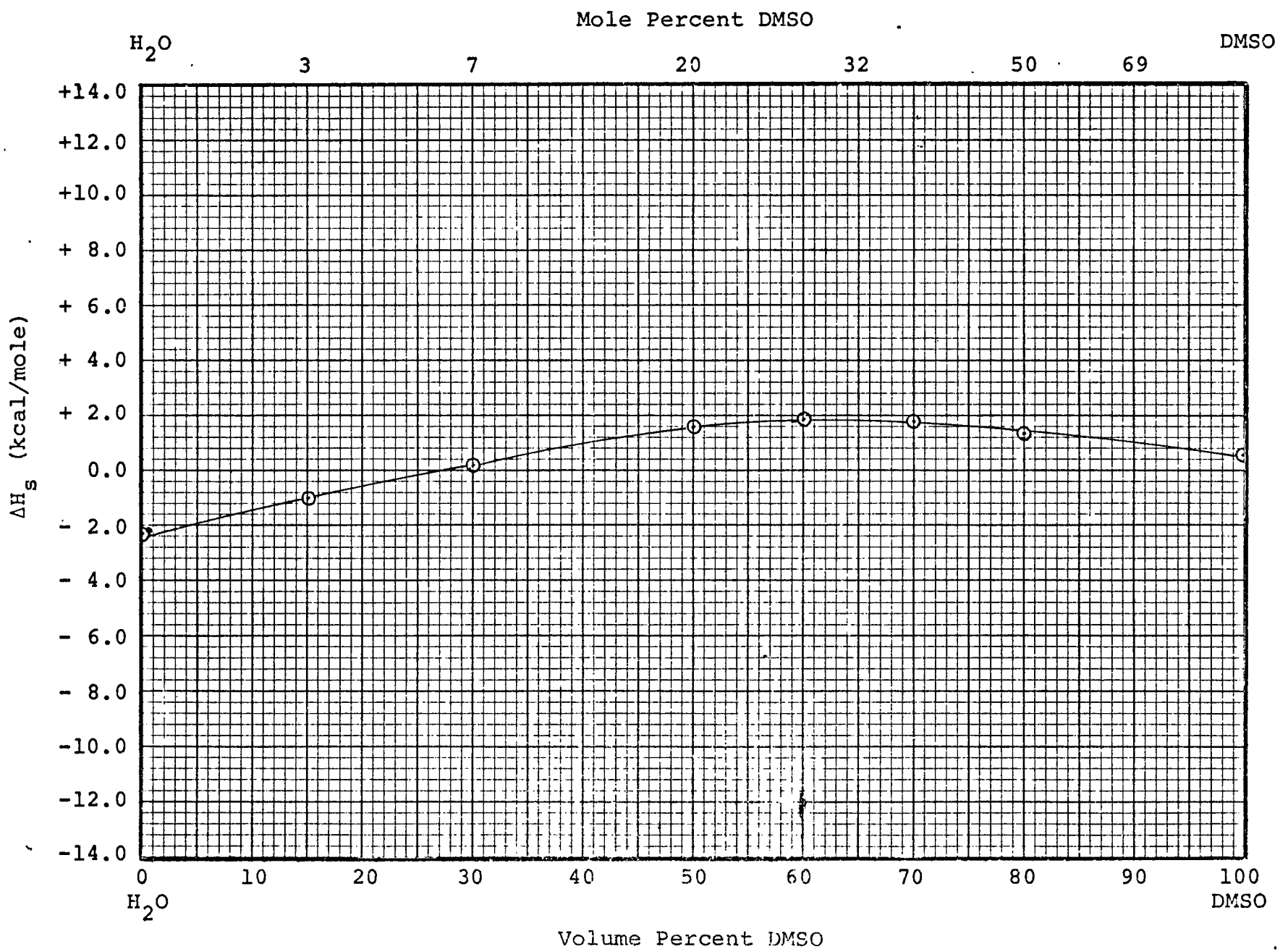

Mole Percent DMSO
H2O
DMSO
3
7
20
32
50
69
+14.0
+12.0
+10.0
+ 8.0
+ 6.0
+ 4.0
+ 2.0
0.0
- 2.0
- 4.0
- 6.0
- 8.0
-10.0
-12.0
-14.0
ΔHs (kcal/mole)
0
10
20
30
40
50
60
70
80
90
100
H2O
DMSO
Volume Percent DMSO

FIGURE 9

PLOT OF ENTHALPY OF SOLUTION VERSUS DMSO CONCENTRATION FOR ETHYL ACETATE


Mole Percent DMSO
H2O
DMSO
3
7
20
32
50
69
+14.0
+12.0
+10.0
+ 8.0
+ 6.0
+ 4.0
+ 2.0
0.0
- 2.0
- 4.0
- 6.0
- 8.0
-10.0
-12.0
-14.0
ΔHs (kcal/mole)
0
10
20
30
40
50
60
70
80
90
100
H2O
DMSO
Volume Percent DMSO

phenylphosphonium ion. Sodium ion is calculated from the appropriate enthalpy values for sodium tetraphenylborate and tetraphenylborate anion. From values for tetrabutylammonium bromide and bromide ion, the transfer value for tetrabutylammonium ion is calculated. The chloride ion transfer value is obtained from tetrabutylammonium chloride and tetrabutylammonium ion. The enthalpy of transfer for iodide ion was determined in two ways: (a) by subtracting enthalpies of transfer for tetrabutylammonium ion from tetrabutylammonium iodide, and (b) by subtracting the enthalpy of transfer for sodium ion from the transfer value for sodium iodide. Both methods should give the same values for the transfer of iodide from water to the appropriate solvent, but they do not. Since the enthalpy of solution of tetrabutylammonium iodide in highly aqueous DMSO is believed to be in error, the values obtained by procedure (b) are believed to be correct and are the ones reported here. Hydroxide ion enthalpy of transfer is obtained from the appropriate data for sodium hydroxide and sodium ion.

Table XXXIII summarizes the single ion enthalpy of transfer values. Table XXXV gives a comparison of these values with the literature values that are available. The transfer value for tetrabutylammonium ion from water to DMSO is 0.7 kcal $mole^{-1}$ lower than the value obtained by Arnett [4] using the tetraphenylarsonium tetraphenylborate assumption. The

TABLE XXXV

COMPARISON OF SINGLE ION ENTHALPIES OF TRANSFER FROM WATER TO DMSO AT 25°

Ion	$H_2O \rightarrow$ DMSO
Na^+	-7.2[a]
	-7.15[b]
	-7.2[c]
$(\underline{n}\text{-}C_4H_9)_4N^+$	5.3[a]
	6.0[d]
$^-B(C_6H_5)_4$	-2.6[a]
	-2.31[b]
	-2.3[c]
Cl^-	4.7[a]
	4.89[b]
	5.1[c]
	4.3[d]
Br^-	1.0[a]
	1.39[b]
	1.1[c]
	1.3[d]
I^-	-2.5[a]
	-2.52[b]
	-2.6[c]
	2.6[d]

[a]This study. [b]Ref. 4. [c]Ref. 49. [d]Ref. 45.

values for other ions are in good agreement with the literature values. The agreement of $\Delta\Delta H$ values based on several different assumptions gives some credibility to the assignment of single ion values. The single ion enthalpies of transfer are plotted versus volume percent of added DMSO in Figures 10-17.

C. SINGLE ION ENTHALPIES OF TRANSFER OF CATIONS

Figure 12 shows that sodium ion is desolvated about 1 kcal $mole^{-1}$ upon the addition of up to 30% by volume DMSO to water. Further addition of DMSO greatly enhances the solvation of the sodium ion. In pure DMSO the sodium ion is solvated 7 kcal $mole^{-1}$ more than in water. Evidence has been presented [39] that the addition of small amounts of DMSO (20-30% by volume) to water increases the water-water interactions. These increased interactions probably occur at the expense of water-sodium ion interactions causing the ion to be desolvated. Upon addition of larger amounts of DMSO, interactions between DMSO and sodium ion (ion-dipole interactions), as well as water-DMSO interactions, begin to occur resulting in enhanced solvation of the sodium ion. The fact that sodium ion is more solvated in pure DMSO than in water is in agreement with the findings of Yao and Bennion [26,27] that small cations interact strongly with DMSO.

FIGURE 10

PLOT OF SINGLE ION ENTHALPY OF TRANSFER VERSUS DMSO CONCENTRATION FOR TETRAPHENYLPHOSPHONIUM AND TETRAPHENYLBORATE IONS

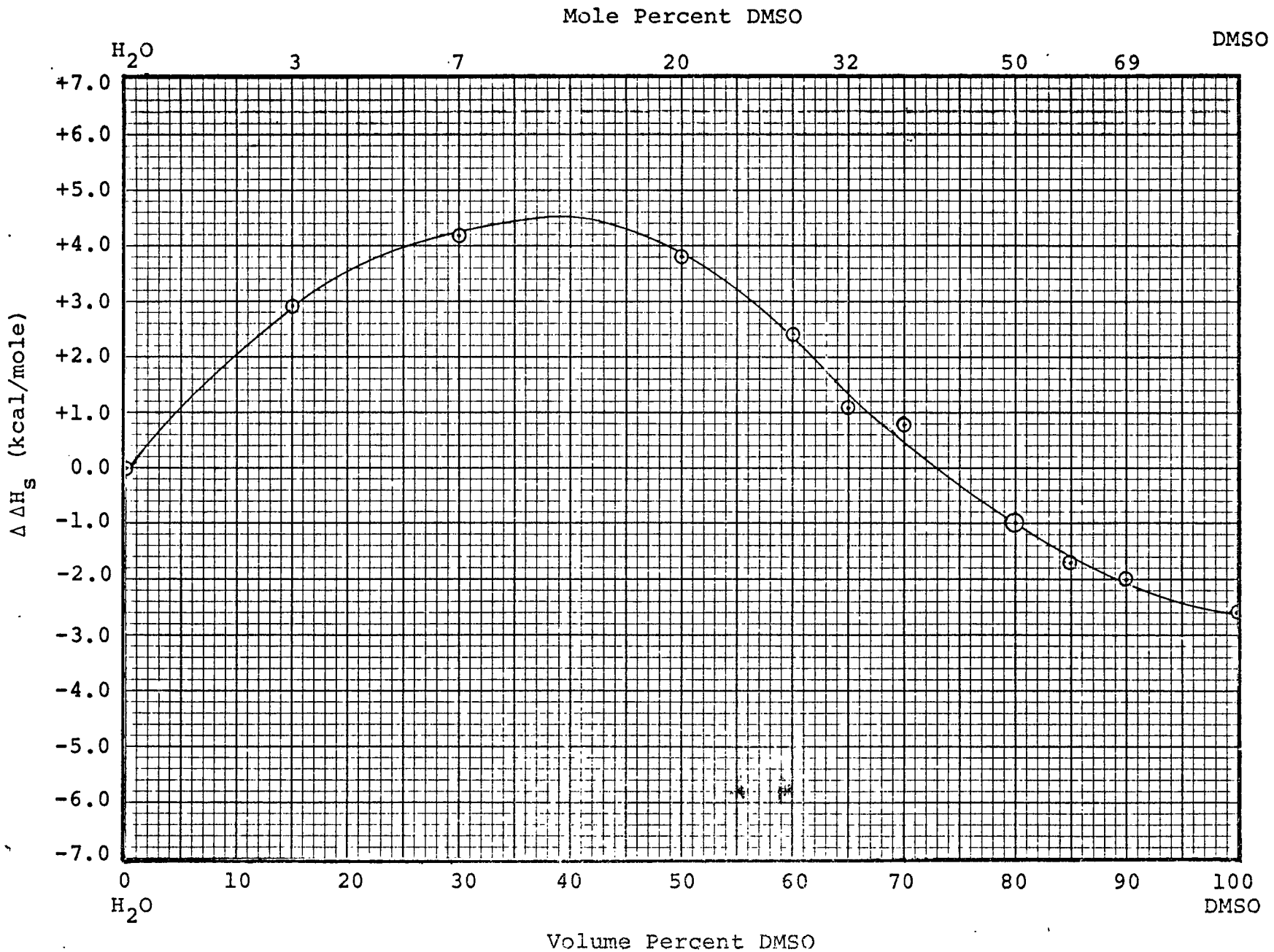

Mole Percent DMSO
H_2O
DMSO
3
7
20
32
50
69
+7.0
+6.0
+5.0
+4.0
+3.0
+2.0
+1.0
0.0
-1.0
-2.0
-3.0
-4.0
-5.0
-6.0
-7.0
$\Delta\Delta H_s$ (kcal/mole)
0
10
20
30
40
50
60
70
80
90
100
H_2O
DMSO
Volume Percent DMSO

FIGURE 11

PLOT OF SINGLE ION ENTHALPY OF TRANSFER VERSUS DMSO CONCENTRATION FOR TETRA-n-BUTYLAMMONIUM ION

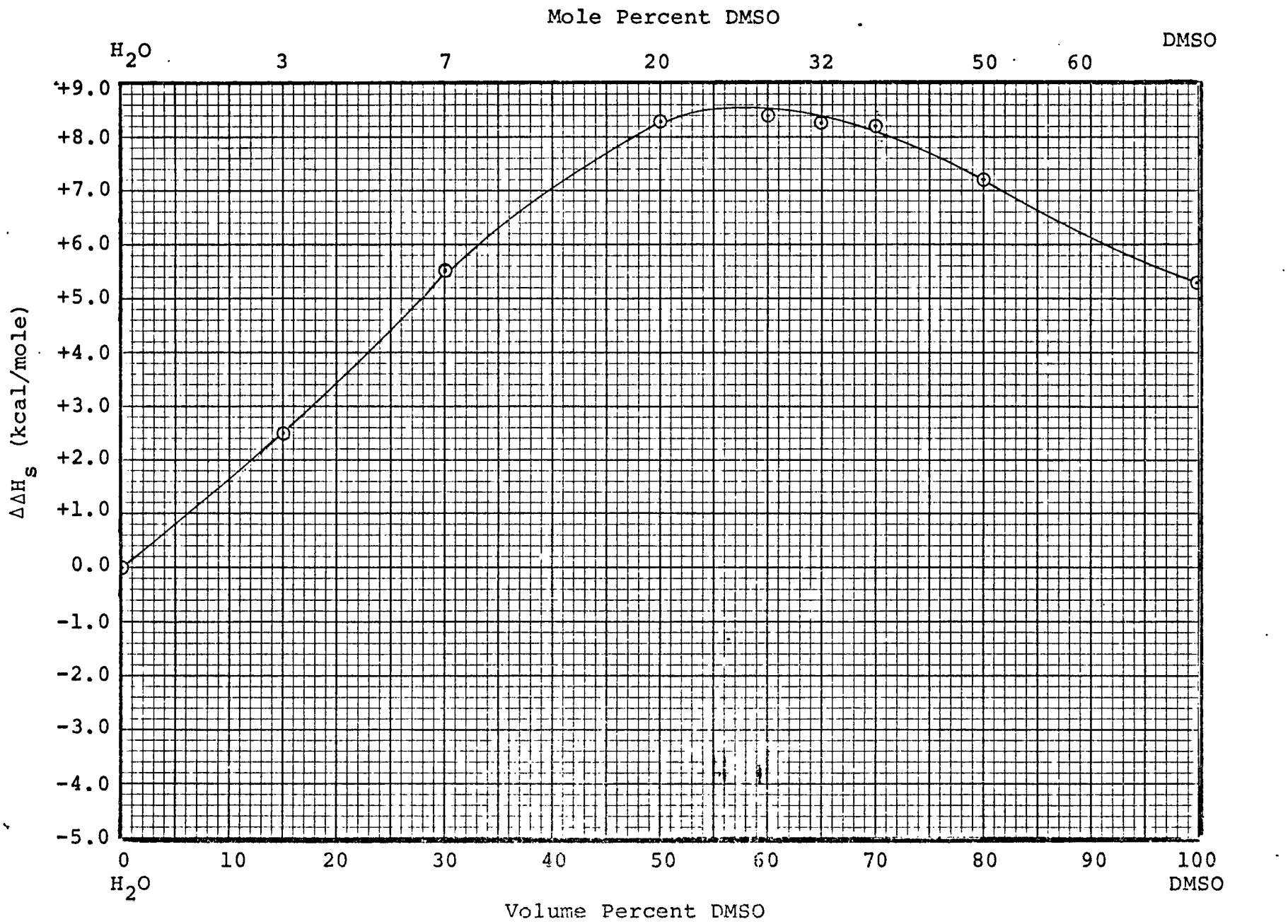

Mole Percent DMSO
H_2O
3
7
20
32
50
60
DMSO
+9.0
+8.0
+7.0
+6.0
+5.0
+4.0
+3.0
+2.0
+1.0
0.0
-1.0
-2.0
-3.0
-4.0
-5.0
$\Delta\Delta H_s$ (kcal/mole)
0
10
20
30
40
50
60
70
80
90
100
H_2O
DMSO
Volume Percent DMSO

FIGURE 12

PLOT OF SINGLE ION ENTHALPY OF TRANSFER VERSUS DMSO CONCENTRATION FOR SODIUM ION

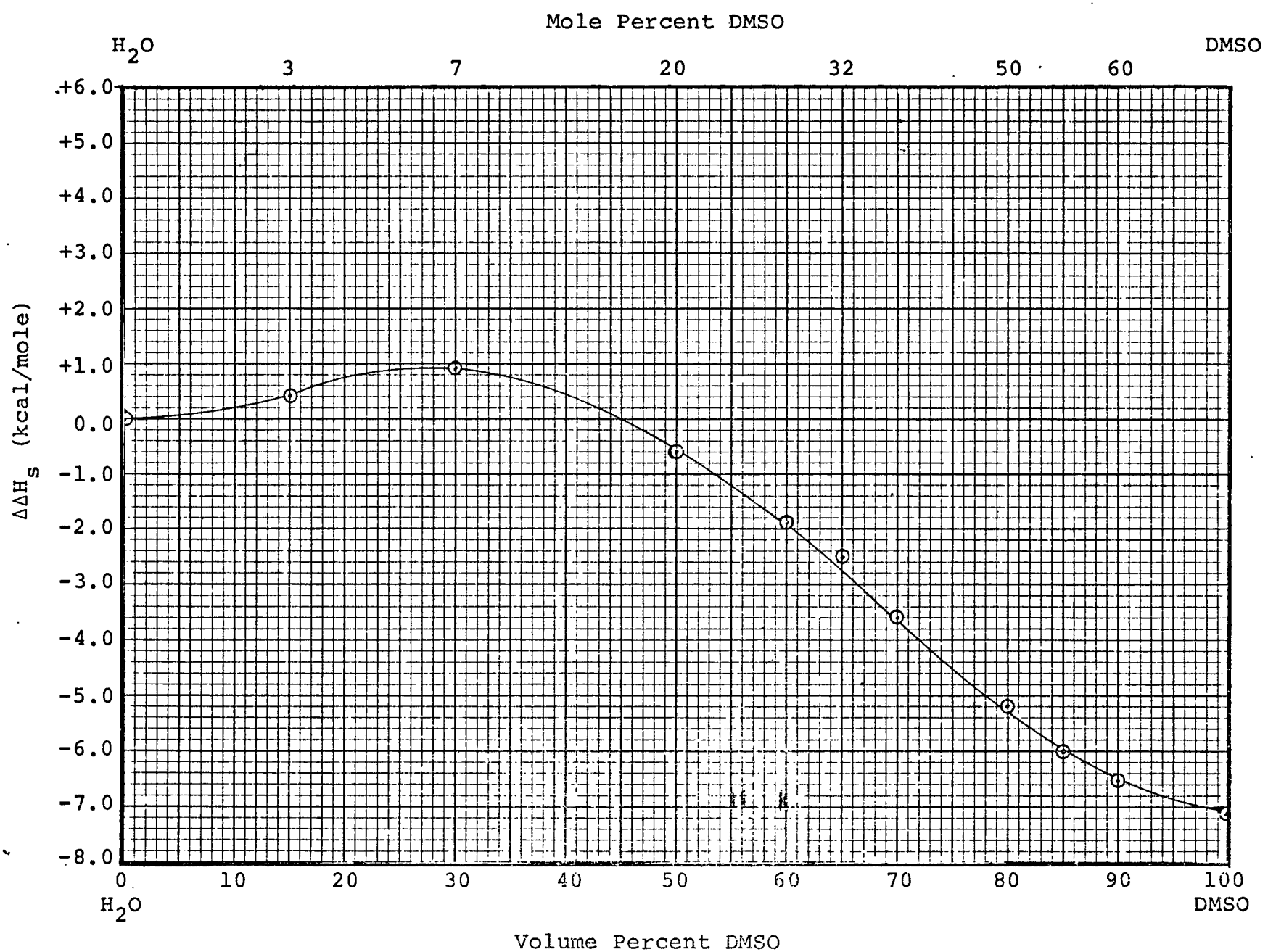

Mole Percent DMSO
H2O
DMSO
3
7
20
32
50
60
+6.0
+5.0
+4.0
+3.0
+2.0
+1.0
0.0
-1.0
-2.0
-3.0
-4.0
-5.0
-6.0
-7.0
-8.0
ΔΔHs (kcal/mole)
0
10
20
30
40
50
60
70
80
90
100
H2O
DMSO
Volume Percent DMSO

FIGURE 13

PLOT OF SINGLE ION ENTHALPY OF TRANSFER VERSUS DMSO CONCENTRATION FOR HYDROXIDE ION

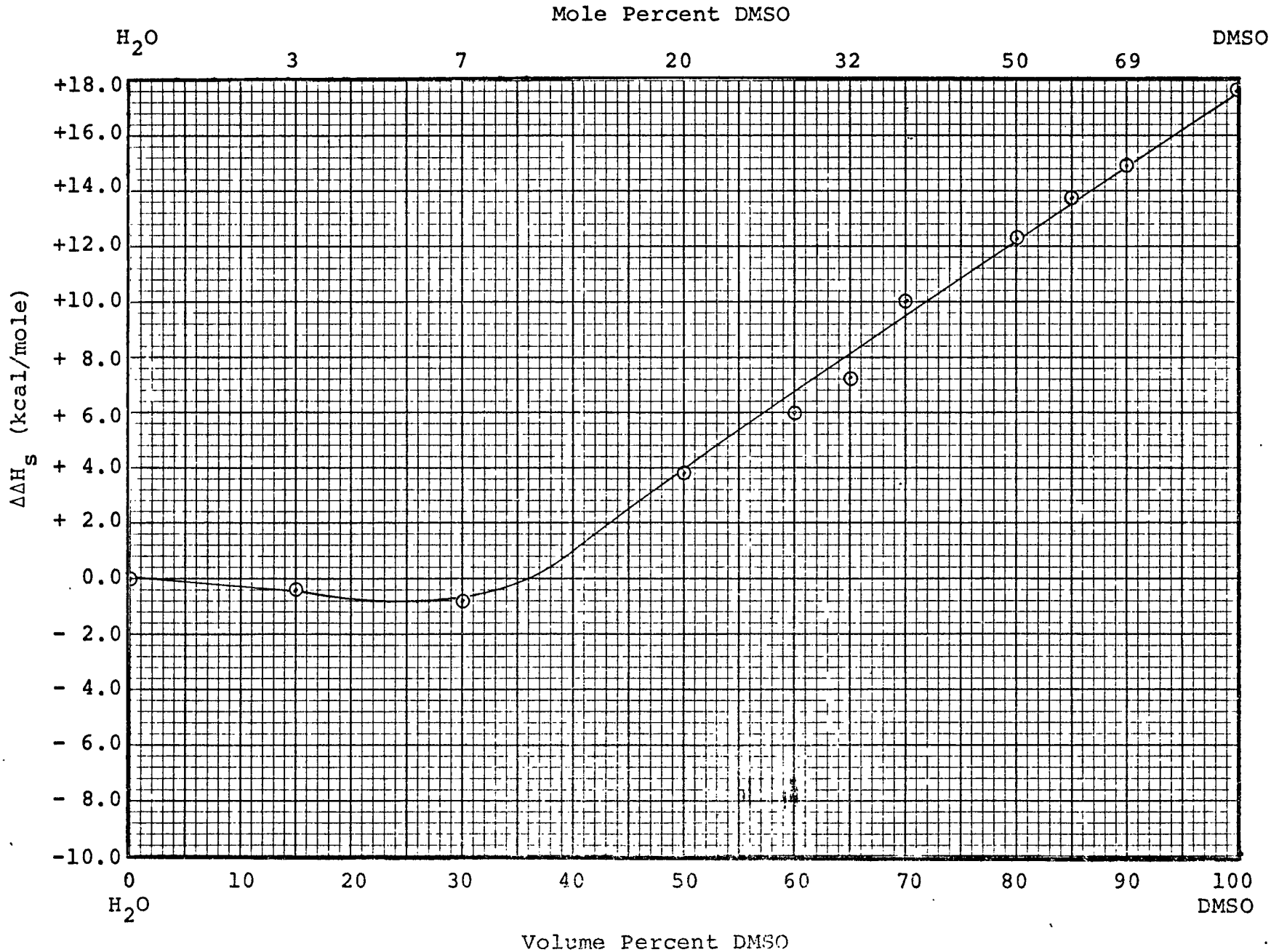

Mole Percent DMSO
H2O
DMSO
3
7
20
32
50
69
+18.0
+16.0
+14.0
+12.0
+10.0
+ 8.0
+ 6.0
+ 4.0
+ 2.0
0.0
- 2.0
- 4.0
- 6.0
- 8.0
-10.0
ΔΔHs (kcal/mole)
0
10
20
30
40
50
60
70
80
90
100
H2O
DMSO
Volume Percent DMSO

FIGURE 14

PLOT OF SINGLE ION ENTHALPY OF TRANSFER VERSUS DMSO CONCENTRATION FOR CHLORIDE ION

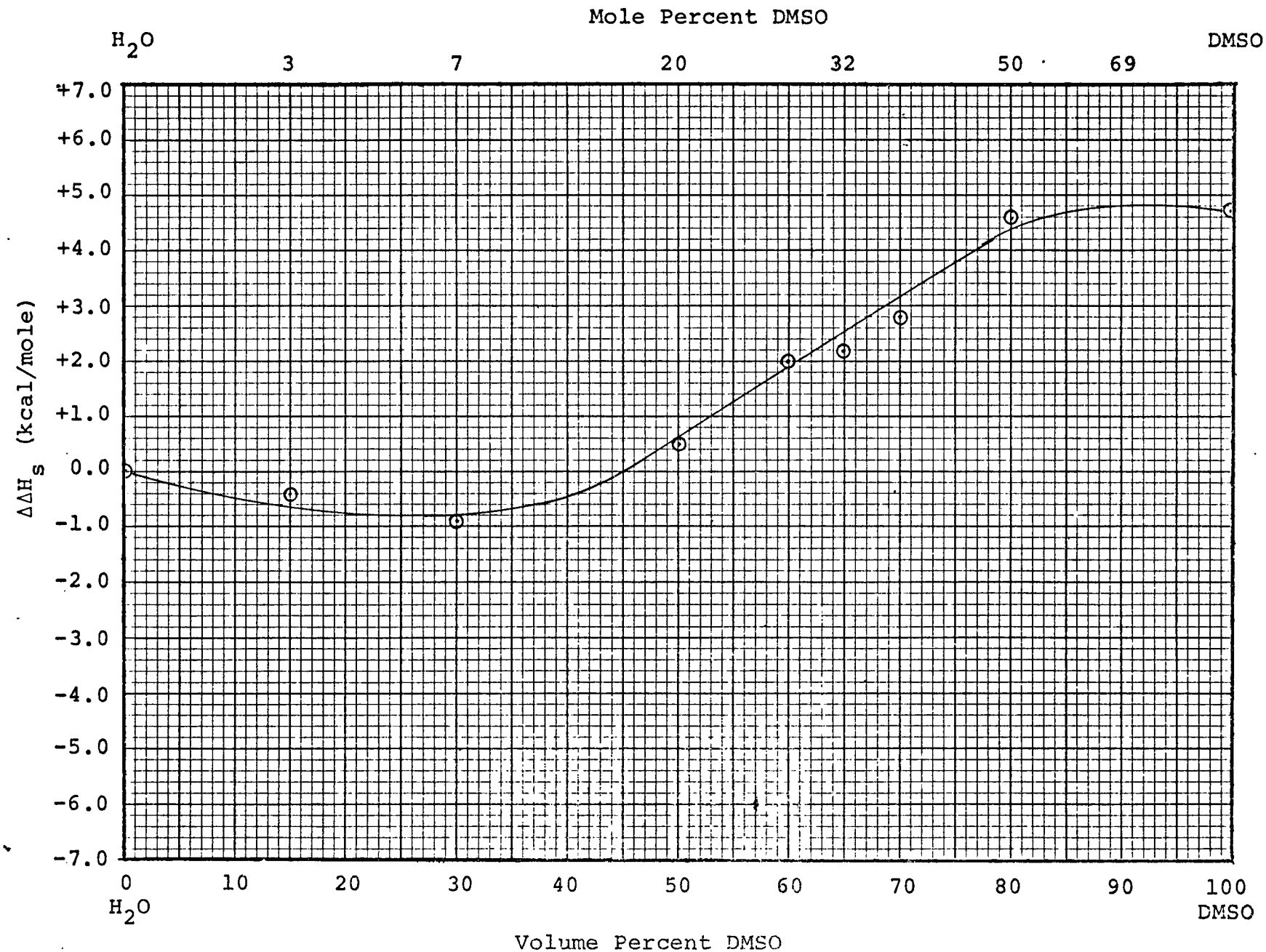

Mole Percent DMSO
H2O
DMSO
3
7
20
32
50
69
+7.0
+6.0
+5.0
+4.0
+3.0
+2.0
+1.0
0.0
-1.0
-2.0
-3.0
-4.0
-5.0
-6.0
-7.0
ΔΔHs (kcal/mole)
0
10
20
30
40
50
60
70
80
90
100
H2O
DMSO
Volume Percent DMSO

FIGURE 15

PLOT OF SINGLE ION ENTHALPY OF TRANSFER VERSUS DMSO CONCENTRATION FOR BROMIDE ION

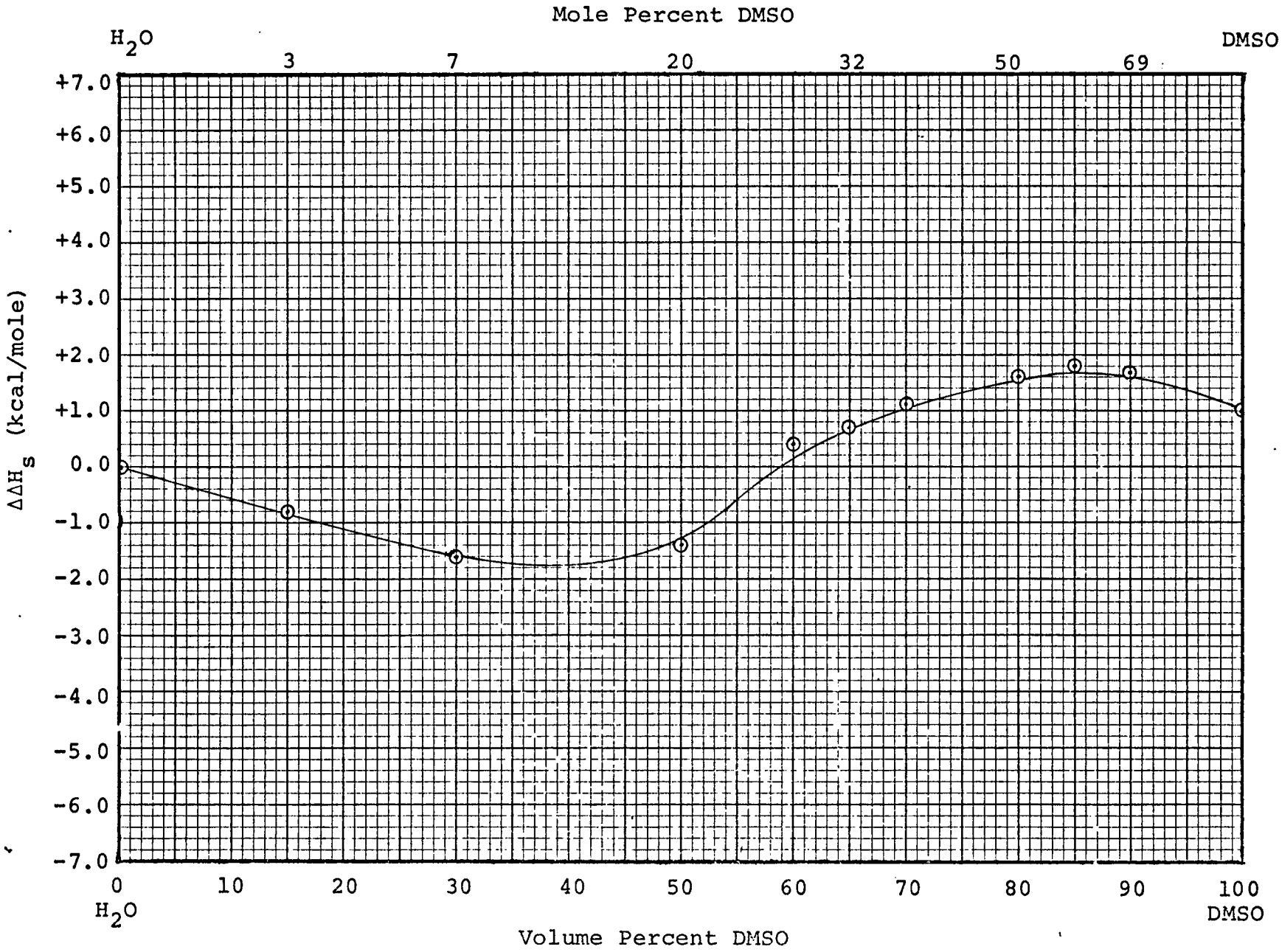

Mole Percent DMSO
H2O
DMSO
3
7
20
32
50
69
+7.0
+6.0
+5.0
+4.0
+3.0
+2.0
+1.0
0.0
-1.0
-2.0
-3.0
-4.0
-5.0
-6.0
-7.0
ΔΔHs (kcal/mole)
0
10
20
30
40
50
60
70
80
90
100
H2O
DMSO
Volume Percent DMSO

FIGURE 16

PLOT OF SINGLE ION ENTHALPY OF TRANSFER VERSUS DMSO CONCENTRATION FOR IODIDE ION

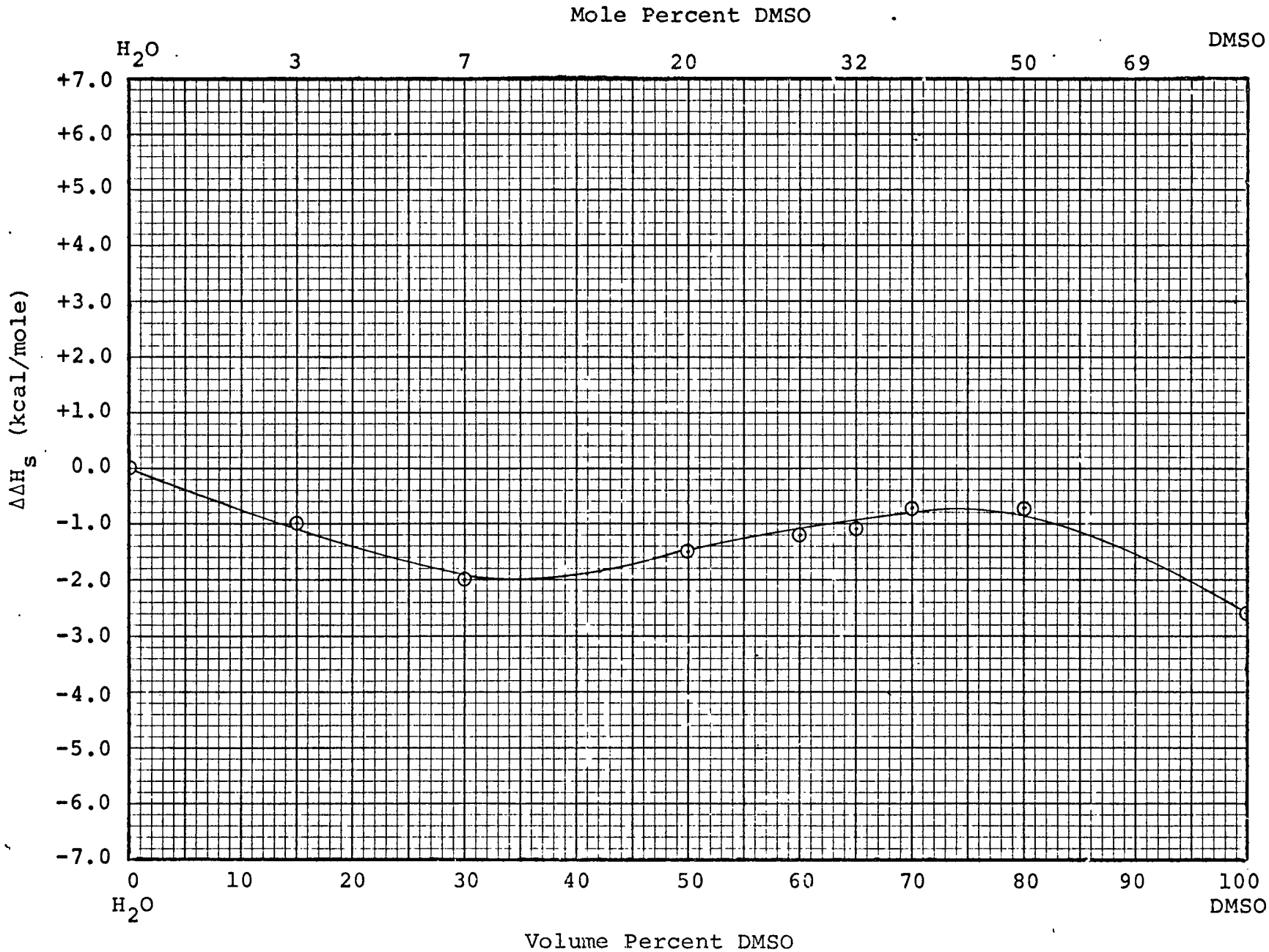
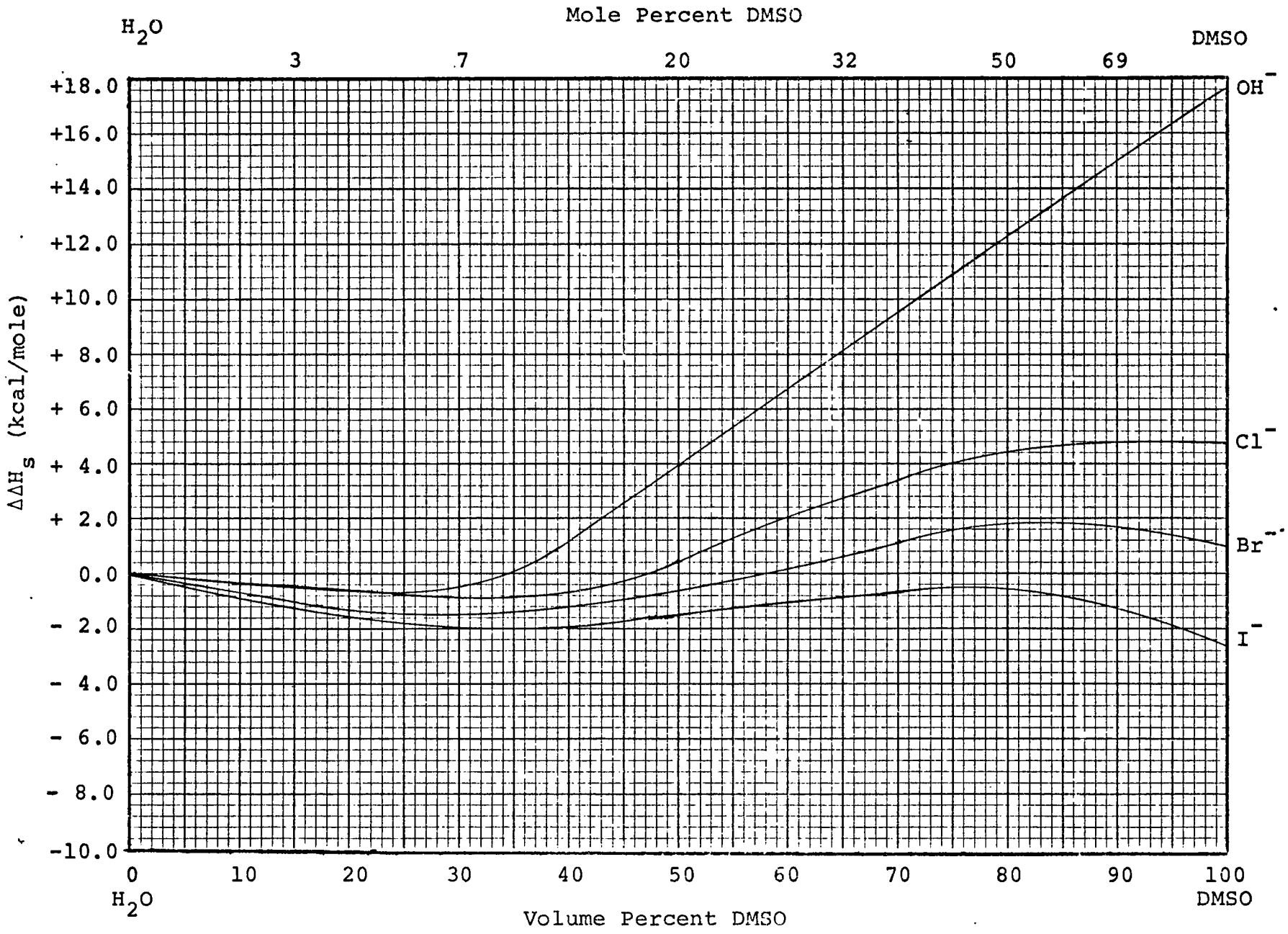

Mole Percent DMSO
H2O
3
7
20
32
50
69
DMSO
+7.0
+6.0
+5.0
+4.0
+3.0
+2.0
+1.0
0.0
-1.0
-2.0
-3.0
-4.0
-5.0
-6.0
-7.0
ΔΔHs (kcal/mole)
0
10
20
30
40
50
60
70
80
90
100
H2O
DMSO
Volume Percent DMSO

FIGURE 17

PLOT OF SINGLE ION ENTHALPY OF TRANSFER VERSUS DMSO CONCENTRATION FOR HYDROXIDE, CHLORIDE, BROMIDE, AND IODIDE IONS


Mole Percent DMSO
H2O
DMSO
3
7
20
32
50
69
+18.0
+16.0
+14.0
+12.0
+10.0
+ 8.0
+ 6.0
+ 4.0
+ 2.0
0.0
- 2.0
- 4.0
- 6.0
- 8.0
-10.0
ΔΔHs (kcal/mole)
OH⁻
Cl⁻
Br⁻
I⁻
0
10
20
30
40
50
60
70
80
90
100
H2O
DMSO
Volume Percent DMSO

The addition of DMSO to water causes a desolvation of the large tetrabutylammonium ion over the entire solvent composition range (Figure 11). A maximum desolvation of about 8 kcal $mole^{-1}$ occurs when the DMSO concentration is about 60% by volume. This solvent composition is very close to the $DMSO \cdot 2H_2O$ solvent composition (65% by volume DMSO) at which aqueous DMSO solutions show maximum solvent structure [33,34]. In solutions containing more than 60% by volume DMSO the tetrabutylammonium ion gains slightly in solvation, but even in pure DMSO the ion is about 5.5 kcal $mole^{-1}$ less solvated than in water. These results are in agreement with the observation by Yao and Bennion [26,27] that large, spherically symmetrical cations with weak surface charge do not interact strongly with DMSO. Aqueous DMSO mixtures are more highly structured than water or DMSO [33-36,38]. Apparently the water-tetrabutylammonium ion interactions are diminished at the expense of water-DMSO interactions upon the addition of DMSO to water.

In the case of sodium ion the loss of water-sodium ion interactions is compensated for by DMSO-sodium ion interactions as the DMSO concentration gradually increases. However, the DMSO-tetrabutylammonium ion interactions are relatively weak and cannot compensate for the loss of water-tetrabutylammonium ion interactions until the DMSO content of the solvent exceeds the $DMSO \cdot 2H_2O$ concentration.

All ions, especially large ones, lose "apparent" solvation as solvent-solvent interactions increase. The ion-solvent interaction itself may be as large as the solvent-solvent interaction, but more energy is needed to make "holes" in the solvent to accommodate the ions. Since large ions need more energy to create "holes" in the solvent than small ions, this also is a reason why tetra-n-butylammonium ion is more desolvated than sodium ion upon the addition of DMSO to water.

D. SINGLE ION ENTHALPIES OF TRANSFER OF ANIONS

Enthalpies of transfer for the anions are plotted versus volume percent of added DMSO in Figures 13-16. For comparison purposes the data for all of the anions is shown in Figure 17. Figure 17 shows that addition of up to 30-40% by volume of DMSO to water causes an increase of about 1-2 kcal $mole^{-1}$ in the solvation of the anions. This increase in solvation of the anions can be explained in terms of the structure promoting effect on water of small amounts of added DMSO. Apparently small amounts of added DMSO cause water to hydrogen bond to itself more strongly [39]. Because the hydrogen bonding is the main interaction responsible for the solvation of small anions in water, the enhanced ability of water to donate hydrogen bonds when small amounts of DMSO are present results in

enhanced solvation of the anions. The mechanism by which small amounts of DMSO promote water structure is not understood.

The addition of larger amounts of DMSO to water causes a very dramatic desolvation of hydroxide anion. The amount of desolvation is approximately a linear function of the added DMSO. Hydroxide anion is desolvated almost 18 kcal $mole^{-1}$ in pure DMSO relative to water.

Haberfield [32] has reported that hydroxide ion is more solvated by 3.5 kcal $mole^{-1}$ upon transfer from 60 mole percent aqueous DMSO to 70 mole percent aqueous DMSO. Haberfield suggests that in DMSO rich solvents hydroxide ion is solvated by "free" DMSO molecules. Hydroxide ion gains in solvation upon transfer from 60 to 70 mole percent aqueous DMSO because there is more "free" DMSO molecules in the 70% solution than in the 60% solution. Our results indicate that hydroxide ion is desolvated upon transfer from 60 to 70 mole percent (85 to 90% by volume) aqueous DMSO by about 1.1 kcal $mole^{-1}$. We feel that this desolvation is due to diminished water content of the solvent. The fact that hydroxide ion is desolvated by 18 kcal $mole^{-1}$ in pure DMSO relative to water suggests that hydroxide ion is strongly solvated by water and/or weakly solvated by DMSO. Hydroxide ion-DMSO interactions may increase slightly upon addition of DMSO, but the increase is not sufficient to compensate for the loss of hydroxide ion-water interactions.

The halide ions are also desolvated with increasing DMSO concentration, but reach a maximum desolvation at about 80% by volume DMSO. In solutions containing greater than 80% DMSO, chloride ion undergoes little change in solvation, bromide ion gains in solvation by about 1 kcal $mole^{-1}$, and iodide ion gains in solvation by about 2 kcal $mole^{-1}$. Solutions containing greater than 80% DMSO contain a molar excess of DMSO, the $DMSO \cdot 2H_2O$ concentration having been reached at 65% by volume DMSO. The solvation behavior of the halide ions in solvent mixtures containing greater than 65% DMSO reflects the fact that DMSO is better able to solvate large, polarizable anions than small anions. For example, in going from 80% by volume DMSO to pure DMSO the small hydroxide ion is desolvated by 6 kcal $mole^{-1}$ while the larger iodide anion is more solvated by about 2 kcal $mole^{-1}$. Upon transfer from water to pure DMSO hydroxide ion is desolvated by 17.7 kcal $mole^{-1}$, chloride ion by 4.7 kcal $mole^{-1}$, and bromide ion by 1.0 kcal $mole^{-1}$, while the iodide ion actually gains 2.5 kcal $mole^{-1}$ in solvation.

E. ENTHALPIES OF TRANSFER FOR ETHYL ACETATE

Ethyl acetate undergoes a gradual desolvation upon the addition of DMSO to water until the DMSO content is about 65% by volume. This is the solvent composition of maximum

structure ($DMSO \cdot 2H_2O$). Further addition of DMSO causes a gradual increase in the solvation of ethyl acetate. Figure 9 shows these results.

F. ENTHALPIES OF TRANSFER OF THE TRANSITION STATE FOR THE BASE-CATALYZED HYDROLYSIS OF ETHYL ACETATE

Tommila and Murto [39], from studies of the kinetics of the base-catalyzed hydrolysis of ethyl acetate in aqueous DMSO, have concluded that anion desolvation is responsible for the observed rate enhancements upon addition of DMSO. Using Tommila and Murto's values for the energy of activation for the reaction at 25°, we have calculated the change in enthalpy of activation for the reaction upon transfer from the solvent water (O) to aqueous DMSO mixtures (S) using the equation,

$$\Delta\Delta H_{O \rightarrow S} = (E-RT)_O - (E-RT)_S = E_O - E_S$$

The change in enthalpy of activation for the reaction upon solvent transfer is used in equation 5 to calculate the change in enthalpy of solvation of the transition state for the reaction. The assumption is made that the enthalpy of activation for the hydrolysis reaction is approximately equal to the activation enthalpy for the first step of the reaction, i.e., the formation of the tetrahedral intermediate. Haberfield [32] has argued that although this assumption is not exact, the difference

between the enthalpy of activation for the transition state and the enthalpy of activation for the formation of the intermediate is small.

Table XXXVI compares the change in solvation of the reactants with the change in solvation of the transition state for the ethyl acetate hydrolysis. The enthalpy of activation for the reaction becomes slightly more negative as DMSO is added to water until the concentration of DMSO is about 20% by volume. In this region the hydroxide ion is gaining in solvation upon addition of DMSO while the ethyl acetate is being desolvated. The ethyl acetate is desolvated to a greater extent than the hydroxide ion gains in solvation, the net result being that the reactants as a whole are being desolvated. This desolvation tends to increase the reaction rate. But the transition state is also being desolvated in this region, although not as much as the reactants, and hence the reaction rate increases only slightly.

Upon the addition of DMSO in amounts greater than 20% by volume, the enthalpy of activation begins to increase. The hydroxide ion begins to be strongly desolvated while the ethyl acetate solvation changes relatively little with further addition of DMSO. The net result is that the reactants as a whole are being rapidly desolvated. One would expect a concurrent decrease in the enthalpy of activation for the reaction.

TABLE XXXVI

ENTHALPY OF TRANSFER FOR THE REACTANTS AND THE TRANSITION STATE FOR THE BASE-CATALYZED HYDROLYSIS OF ETHYL ACETATE AT 25° (REF. SOLVENT: WATER)

% DMSO[a] (vol)	E[b] (kcal mole^{-1})	$\Delta\Delta H^{\ddagger}$ (kcal mole^{-1})	$\Delta\Delta H^{-}OH^{c}$ (kcal mole^{-1})	$\Delta\Delta H$ EtOAc[c] (kcal mole^{-1})	$\Sigma\Delta\Delta H_s^r$ (kcal mole^{-1})	$\Delta\Delta H^t$ (kcal mole^{-1})
H_2O	11.40	---	---	---	---	---
10	11.21	-0.19	-0.3[d]	0.9[d]	0.6	0.4
20	11.01	-0.39	-0.8[d]	1.7[d]	0.9	0.5
40	11.18	-0.22	1.0[d]	3.3[d]	4.3	4.1
60	11.68	0.28	6.0	4.21	10.2	10.5
80	12.32	0.92	12.25	3.75	16.0	16.9
84.5	12.45	1.05	13.4[d]	3.6[d]	17.0	18.0

[a]This is ml. water/liter solvent for data taken from Ref. [30]. [b]Ref. 30. [c]This study. [d]These values were obtained graphically.

In fact the enthalpy of activation actually increases in this region due to the fact that the transition state is being desolvated to a greater extent than the sum of the reactants. These results indicate that anion desolvation alone is not responsible for the observed rate accelerations.

In agreement with our results, Roberts [31] has concluded from kinetic studies of the effect of added DMSO on the base-catalyzed hydrolysis of branched and straight-chain esters that desolvation of the anion is not the main factor responsible for the solvent effects on the rates. Roberts believes that the ability of DMSO to solvate the transition state is responsible for the rate enhancements upon the addition of DMSO. From Roberts' kinetic data for base-catalyzed ethyl acetate hydrolysis at 25° we have calculated the change in transition state solvation upon transfer from 30.5% by volume aqueous DMSO to more DMSO rich solvents (Table XXXVII). Roberts found that the rate of the hydrolysis reaction increases with increasing solvent DMSO concentration. This is in agreement with the results of Tommila and Murto [39]. The data in Table XXXVII show that increased solvation of the transition state is not responsible for the rate increases. In fact the transition state is desolvated with increasing DMSO concentration, and in each solvent mixture the amount of desolvation of the transition state is greater than the combined desolvation of the reactants.

TABLE XXXVII

ENTHALPY OF TRANSFER FOR REACTANTS AND TRANSITION STATE FOR THE BASE-CATALYZED HYDROLYSIS OF ETHYL ACETATE AT 25° (REF. SOLVENT: 30.5% AQUEOUS DMSO)

% DMSO (vol)	$\Delta H^{\ddagger a}$ (kcal mole^{-1})	$\Delta\Delta H^{\ddagger}$ (kcal mole^{-1})	$\Delta\Delta H\ ^{-}OH^{b}$ (kcal mole^{-1})	$\Delta\Delta H$ EtOAc (kcal mole^{-1})	$\Sigma\ \Delta\Delta H_s^r$ (kcal mole^{-1})	$\Delta\Delta H^t$ (kcal mole^{-1})
30.5	8.60	---	---	---	---	---
50	9.20	0.6	4.4	1.4	5.8	6.4
60	9.40	0.8	6.8	1.7	8.5	9.3
65	9.70	1.1	8.1	1.8	9.9	11.0
70	9.60	1.0	10.8	1.6	12.4	13.4
75	8.10	-0.5	11.6[c]	1.4[c]	13.0	12.5
80	9.40	0.8	13.0	1.3	14.3	15.1
85	10.80	2.2	14.5	1.0[c]	15.5	17.7

[a]Ref. 31. [b]This study. [c]Obtained graphically.

Certainly desolvation of the hydroxide anion upon the addition of DMSO to water is an important contributing factor to the observed increase in the rate of base-catalyzed ethyl acetate hydrolysis. But there are other important contributing factors. In aqueous DMSO solutions containing up to about 20% by volume DMSO the slight rate increases (relative to water) observed by Tommila and Murto [39] occur because the transition state is less desolvated than the reactants. In aqueous DMSO solutions containing greater than 20% by volume DMSO the transition state is more desolvated than the reactants. Since at high DMSO content the reaction rate increases despite an increase in the enthalpy of activation, there must be a simultaneous and larger increase in the entropy of activation. Apparently the greater change in entropy of activation upon the addition of DMSO is also responsible for the observed rate enhancements.

The change in entropy of solvation for ethyl acetate has been calculated from the change in solvent activity coefficients of ethyl acetate upon addition of DMSO to water reported by Cox and McTigue [52]. The solvent activity coefficients were converted to free energies of transfer using the equation

$$\Delta G = 2.303 \log {}^{w}\gamma^{s}$$

and the $T\Delta\Delta S$ term was calculated from the free energies and enthalpies of transfer. Table XXXVIII shows these results.

TABLE XXXVIII

FREE ENERGY, ENTHALPY, AND ENTROPY OF TRANSFER OF ETHYL ACETATE FROM WATER TO AQUEOUS DMSO AT 25°

% DMSO (vol)	Log $^{w}\gamma^{s}$ [a]	$\Delta\Delta G$[b] (kcal mole^{-1})	$\Delta\Delta H$[c] (kcal mole^{-1})	$T\Delta\Delta S$[d] (kcal mole^{-1})
0	0.00	0.00	0.00	0.00
30.5	0.088	0.12	2.46	2.34
50	0.105	0.14	3.85	3.71
63	0.024	0.03	4.2[e]	4.17
72.5	-0.134	-0.18	4.0[e]	4.18
80	-0.270	-0.40	3.75	4.15
85	-0.421	-0.57	3.5[e]	3.9
89	-0.567	-0.77	3.3[e]	4.0
94	-0.675	-0.92	3.1[e]	4.0
97.5	-0.755	-1.0	2.9[e]	3.9

[a]Ref. 52. [b]Calculated from $\Delta\Delta G = 2.303\ RT \log\ ^{w}\gamma^{s}$. [c]This study. [d]Calculated from $\Delta\Delta G = \Delta\Delta H - T\Delta\Delta S$. [e]These values obtained graphically.

The change in entropy of solvation of ethyl acetate upon the addition of DMSO to water is large, and in solutions containing greater than about 50% by volume of DMSO the entropy term is larger than the enthalpy term.

Unfortunately solvent activity coefficients for hydroxide ion, and for the transition state of base-catalyzed hydrolysis of ethyl acetate in aqueous DMSO are not available. Consequently the entropy contributions to solvation of these species in aqueous DMSO cannot be determined.

Tables XXXVI and XXXVII reveal another interesting and extremely important phenomenon. In the transfer from water to all aqueous DMSO mixtures, the transition state is more desolvated than is the hydroxide ion. Since DMSO is better able to solvate large polarizable anions than small highly charged anions, this result is unexpected. A priori this result suggests that the transition state for base-catalyzed ethyl acetate hydrolysis has a more highly localized charge than does hydroxide ion. But the comparative size of the transition state and the hydroxide ion should also be considered. Perhaps the greater "apparent" desolvation of the transition state relative to the hydroxide ion is due not to weaker solvent-solute interactions but to a greater endothermal contribution to $\Delta\Delta H_s$ resulting from the energy necessary to make a "hole" in the solvent. More energy is required to make the "large

hole" in the solvent for the transition state than is required to make the "small hole" for the hydroxide ion. This explanation is consistent with the fact that ethyl acetate itself is desolvated upon the addition of DMSO to water.

From the results of this study the following general conclusions can be made: (1) The solvation in aqueous DMSO of ions that interact only weakly with either water or DMSO [e.g. $(n\text{-}C_4H_9)N^+$] is highly dependent on the amount of structure of the aqueous DMSO solvent. An increase in structure of the solvent leads to decrease in solvation of these ions; (2) The solvation of ions that interact strongly with water but not with DMSO (small anions) is less sensitive to the structure of aqueous DMSO solvents, although the ions are somewhat desolvated as the solvent structure increases; (3) The solution of ions that interact strongly with DMSO (e.g., Na^+) increases as the DMSO concentration increases. The solvation of these ions is not very sensitive to the solvent structure; (4) Changes in entropy of solvation, as well as enthalpy of solvation, of the reactants and the transition state is an important contributing factor to the observed effect of added DMSO on the rate of base-catalyzed hydrolysis of ethyl acetate.

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