Enthalpies of Solution of Selected Electrolytes in Sulfolane and in Acetonitrile

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An isoperibol solution calorimeter has been employed to measure enthalpies of solution of selected alkali metal and tetraalkylammonium halides in sulfolane at 30.00 °C and in acetonitrile at 25.00 °C. Enthalpies of solution have also been measured for $NaClO_4$ in sulfolane. All measurements were made at concentrations <0.01 *m* and have been corrected to standard state conditions. Within limits of experimental error the concentration dependence of the data agrees with the calculated Debye–Hückel limiting slopes. Sulfolane exhibits a negative limiting slope, which, to the authors' knowledge, is the first time a pure solvent showing this characteristic has been reported. Standard enthalpies of transfer of the electrolytes from acetonitrile (AN) to sulfolane (TMS), $\Delta H^\circ_{TMS \leftarrow AN}$, are negative for all electrolytes examined, except for lithium salts, which exhibit large positive values for $\Delta H^\circ_{TMS \leftarrow AN}$. The results are discussed in terms of the suitability of the solvents for use as reference solvents.

Several papers have appeared in recent years reporting enthalpies of transfer of electrolytes from water to various protic and aprotic solvents (*2, 3, 5, 8, 12, 23*). A primary intent of these studies has been to employ transfer enthalpies of ions from water to an "ideal" solvent as a probe for examining the structural effects of ions on aqueous solutions. The major problem is that the "ideal" solvent does not exist, and one is reduced to finding as ideal a solvent as possible as a reference solvent, that is, a solvent with a minimal number of specific interactions with ions. Wu and Friedman (*23*) have suggested propylene carbonate (PC) as a reference solvent, and Choux and Benoit (*5*) examined transfer enthalpies of ions from PC to a series of solvents. Similar studies have been made on *N,N*-dimethylformamide (DMF) in this laboratory (*3*), with the hope that this solvent would be a useful reference solvent. The difficulty in any study involving transfer functions is knowing which solvent is exhibiting specific interactions, the proposed reference solvent or the working solvent. In order to find a useful reference, it would appear that one should examine several potential solvents, each having properties that suggest a lack of specific interactions. By comparing and minimizing the transfer functions, one can presumably find a solvent nearly devoid of specific interactions. Clearly aprotic solvents will fit this category better than protic solvents.

Two aprotic solvents of potential use as reference solvents and for which only a few data exist are sulfolane (TMS) (*5*) and acetonitrile (AN) (*1, 4, 13*). The purpose of this paper is to report enthalpies of solution for several additional electrolytes in these solvents, to reexamine some previously reported values of some key electrolytes, and to obtain enthalpies of transfer of electrolytes between these solvents. The choice of electrolytes chosen for study was dictated by the desire to obtain accurate enthalpy data on the alkali metal, halide, and tetraalkylammonium ions in these solvents, limited primarily by the solubility and rapidity of solution of the corresponding salts.

Experimental Section

Materials. Sulfolane (Phillips Petroleum Co.) was treated first with NaOH pellets and then 3 Å molecular sieves, and finally distilled at 0.2 Torr through a glass-packed fractionating column. A small stream of dry nitrogen was bubbled through the solvent during the distillation. The middle fraction of about 80%, and distilling at 80 °C, was collected. Karl Fisher titrations indicated the water content to be less than 0.007%.

Acetonitrile was purified by two methods. The first was that of Coetzee and co-workers (*6*), in which the solvent is treated with CaH_2, fractionally distilled from P_2O_5, refluxed for several hours over CaH_2, and finally fractionally distilled slowly at 80.5 °C. The water content after this treatment was about 0.003%. The second treatment was a modification of the method of Tuan and Fuoss (*21*). Acetonitrile was refluxed overnight with Drierite, transferred to CaH_2, and fractionally distilled under nitrogen at atmospheric pressure. The middle fraction of about 80% and boiling at 80.5 °C was collected. The water content was about 0.005%. In both cases the solvent was stored under dry nitrogen. Enthalpies of solution were independent of the method of solvent preparation, and consequently the latter method of preparation was generally employed.

LiBr was recrystallized from water, air-dried for 10 h at 100 °C, and finally dried at 190 °C in a vacuum oven fitted with a liquid N_2 trap.

LiI was prepared by reacting Li_2CO_3 with excess concentrated reagent grade HI. The solution was evaporated slowly by passing dry N_2 over it. The resulting LiI was recrystallized from water and collected on a sintered glass funnel, the whole process being performed under a N_2 atmosphere. It was dried in a vacuum desiccator over P_2O_5 overnight, and then heated in a vacuum oven for 24 h at 150 °C.

Reagent grade NaI and KI were recrystallized from water, dried in a vacuum desiccator, and heated in a vacuum oven for 24 h at 150 °C. CsI (99.95%, supplied by Henley and Co.) was used without further purification, except for drying in a vacuum oven overnight at 150 °C. $NaClO_4$ was purified by methods described previously (*16*).

Me_4NBr and Me_4NI were recrystallized twice from water–methanol mixtures, Pr_4NBr was recrystallized three times from methanol–ether mixtures, and Bu_4NBr was recrystallized three times from acetone–ether mixtures. After preliminary drying, all of the salts, except Bu_4NBr, were dried at 120 °C over night in a vacuum oven, fitted with a liquid N_2 trap. Bu_4NBr was dried at 90 °C.

Apparatus and Procedure

The calorimeter and general techniques have been reported elsewhere (*9, 20*). The most significant procedural change involved the preparation of the sample ampoules. These were sealed under N_2 at 1 atm, except for the iodide salts which were sealed under vacuum to avoid partial decomposition through excessive heating. Salts that tended to decompose were sealed in the ampoules while the portion containing the salt was submerged in ice water. Heats of ampoule breaking, which were smaller for the ampoules sealed at atmospheric pressure, were corrected for in all measurements.

Results and Discussion

Tables I and II list enthalpies of solution for the electrolytes in sulfolane at 30.00 °C and in acetonitrile at 25.00 °C. All

Table I. Enthalpies of Solution of Electrolytes in Sulfolane at 30.00 °C

$10^3 m$	ΔH_s (kcal mol^{-1})	$\Delta H_s°$ (kcal mol^{-1})
	LiBr	
0.3670	−6.606	−6.592
0.5669	−6.590	−6.572
0.8507	−6.614	−6.592
1.0107	−6.608	−6.584
1.3482	−6.595	−6.567
1.7182	−6.615	−6.584
2.0368	−6.608	−6.574
	LiI	
0.4370	−14.231	−14.215
0.9767	−14.346	−14.322
1.1525	−14.324	−14.298
1.5822	−14.298	−14.267
2.0540	−14.370	−14.336
	NaI	
0.3519	−8.036	−8.022
0.5125	−8.050	−8.033
0.7324	−8.063	−8.042
0.8419	−8.052	−8.030
1.2136	−8.047	−8.021
	KI	
0.1196	−3.961	−3.953
0.2223	−3.972	−3.961
0.2879	−3.950	−3.937
0.3291	−3.948	−3.934
0.6911	−3.964	−3.944
1.1342	−3.956	−3.930
1.2410	−3.973	−3.946
1.5183	−3.964	−3.934
	CsI	
0.2914	−0.829	−0.816
0.3528	−0.834	−0.820
0.3981	−0.819	−0.804
0.4305	−0.832	−0.816
0.5521	−0.825	−0.807
0.6092	−0.842	−0.823
0.8371	−0.831	−0.809
1.1720	−0.838	−0.812
	$NaClO_4$	
0.3611	−5.248	−5.234
0.5160	−5.210	−5.193
0.7406	−5.234	−5.213
0.8372	−5.214	−5.192
0.8658	−5.211	−5.189
1.1293	−5.240	−5.215
1.2304	−5.237	−5.210
1.7321	−5.228	−5.196
2.1612	−5.244	−5.209
2.7505	−5.252	−5.212
	Me_4NI	
0.2412	4.325	4.337
0.3548	4.364	4.378
0.5121	4.302	4.319
0.6629	4.353	4.373
0.8089	4.321	4.343
	n-Pr_4NBr	
0.1406	5.163	5.172
0.3522	5.154	5.168
0.5730	5.161	5.179
0.7125	5.148	5.168
0.7494	5.146	5.167
0.8579	5.150	5.172
	n-Bu_4NBr	
0.4347	6.126	6.142
0.7519	6.116	6.137
1.2629	6.119	6.146
1.6058	6.114	6.144

Table II. Enthalpies of Solution of Electrolytes in Acetonitrile at 25.00 °C

$10^3 m$	ΔH_s (kcal mol^{-1})	$\Delta H_s°$ (kcal mol^{-1})
	LiBr	
0.8823	−9.497	−9.546
1.0607	−9.488	−9.542
1.2979	−9.453	−9.513
1.9803	−9.473	−9.547
2.3047	−9.463	−9.543
2.6865	−9.468	−9.554
3.2930	−9.439	−9.534
	NaI	
1.2270	−6.918	−6.976
1.6565	−6.929	−6.996
2.1539	−6.899	−6.976
3.3178	−6.868	−6.963
3.8329	−6.872	−6.975
	KI	
0.5870	−2.443	−2.483
1.4969	−2.422	−2.486
2.6774	−2.402	−2.488
3.9370	−2.381	−2.485
	CsI	
0.6664	0.071	0.028
1.0064	0.091	0.039
1.8908	0.092	0.020
2.9602	0.117	0.027
3.6382	0.121	0.021
	Me_4NBr	
0.3925	4.500	4.467
1.0300	4.511	4.458
2.1569	4.535	4.458
2.4367	4.560	4.478

measurements were made at concentrations of <0.01 *m*. Within the limits of experimental error the data conformed to the simple Debye–Hückel equation

$$\Delta H_s = \Delta H_s° + \tfrac{2}{3}\delta_H m^{1/2} \qquad (1)$$

and this equation was employed to correct the measured enthalpies at each concentration to the standard state enthalpies, $\Delta H_s°$. These are listed in the third column of Tables I and II.

Density and dielectric constant data used in calculating the Debye–Hückel limiting slope, δ_H, for sulfolane are from Lamanna and co-workers (*14, 15*), and at 30.00 °C this slope is −1139.1 cal kg$^{1/2}$ mol$^{-3/2}$. In order to calculate δ_H for acetonitrile, a composite of reported densities and dielectric constants from Karnes (*10*), Minc and Werblan (*17*), Danyluk (*7*), and Walden (*22*) were employed. The resultant value of δ_H at 25.00 °C is 2484 cal kg$^{1/2}$ mol$^{-3/2}$. As far as the authors know, sulfolane is the first pure solvent for which a negative limiting slope for enthalpies has been observed, and the measured enthalpies of solution confirm the theoretically calculated value within the limits of error.

Table III lists the average of the standard enthalpies of solution and their standard deviations for electrolytes in sulfolane and acetonitrile. For comparison, previously reported values are listed where they are available. With the exception of NaI in sulfolane, the data agree within about 0.2 kcal/mol, which is reasonable in view of the experimental difficulties encountered in these solvent systems.

Both TMS and AN exhibit properties that make them potentially useful reference solvents. Both are weakly basic, both are aprotic, and both solvate cations and anions poorly (*11, 18*). Furthermore, the dielectric constants of these two solvents have a ratio (41.29/36.77 = 1.12) within about 10% of the ratio of their dipole moments (4.81/3.92 = 1.23), indicating no significant orientations or interactions within the pure solvents, other than

Table III. Standard Enthalpies of Solution of Electrolytes in Sulfolane at 30.00 °C and in Acetonitrile at 25.00 °C, and the Enthalpy of Transfer from Acetonitrile to Sulfolane

Electrolyte	ΔH_s° (kcal mol^{-1})[f] TMS	AN	$\Delta H^\circ_{\mathrm{TMS}\leftarrow\mathrm{AN}}$ (kcal mol^{-1})
LiBr	−6.58 ± 0.01	−9.54 ± 0.01	2.96
LiI	−14.29 ± 0.05	−16.89[b]	2.60
NaI	−8.03 ± 0.01 (−7.41)[a]	−6.98 ± 0.01 (−6.88)[c]	−1.05
KI	−3.94 ± 0.01	−2.486 ± 0.002 (−2.33)[d]	−1.45
CsI	−0.81 ± 0.01	0.03 ± 0.01	−0.84
Me_4NBr		4.47 ± 0.01 (4.21)[e]	
Me_4NI	4.35 ± 0.03	4.59[d]	−0.24
$NaClO_4$	−5.21 ± 0.01 (−5.40)[a]	−4.15[c]	−1.06
n-Pr_4NBr	5.17 ± 0.01		
n-Bu_4NBr	6.142 ± 0.004		

[a] Reference 5. [b] Calculated from ionic enthalpies of transfer of Li^+ and I^- from water to AN and the known enthalpy of solution of LiI in water. The ionic enthalpies of transfer from water to AN were obtained from the enthalpy data in the above table and the known enthalpies of solution of the corresponding salts in water. [c] Reference 13. [d] Reference 1. [e] Reference 4. [f] Uncertainties are standard deviations from the mean.

those expected from normal dipole–dipole interactions.

If neither solvent exhibits specific interactions with ions, then $\Delta H^\circ_{\mathrm{TMS}\leftarrow\mathrm{AN}}$ should be a smoothly varying function of radius for all ions transferred. However, since the dielectric constants and their temperature derivatives for these solvents are not too widely different, one might expect the dependence of $\Delta H^\circ_{\mathrm{TMS}\leftarrow\mathrm{AN}}$ on ionic radius to be small. From the iodide salts in Table III it is clear that no simple relationship involving radius exists. However, with the exception of the lithium salts and Me_4NI, $\Delta H^\circ_{\mathrm{TMS}\leftarrow\mathrm{AN}}$ for all of the electrolytes are within about 0.3 kcal of a constant value of −1.1 kcal/mol. This spread is considerably larger than the standard deviations of the measurements, and probably indicates specific interactions of the various ions with one or both of the solvents. On the other hand, if our results have absolute errors comparable to the deviations among various workers, then the 0.3 kcal spread is of no significance. What is significant from the data in Table III is that the lithium salts are considerably different than any of the other salts, indicating that Li^+ is either strongly complexed to AN or weakly complexed to TMS, or both, relative to other cations. If neither solvent showed specific interactions, this difference would not occur. We suggest that the large $\Delta H^\circ_{\mathrm{TMS}\leftarrow\mathrm{AN}}$ values for the lithium salts are the result of a greater change in solvation number for Li^+ relative to the other ions when they are transferred from AN to TMS. Spiro (*19*), on the basis of conductance measurements, has assigned tentative solvation numbers for some of the alkali metal ions in AN and TMS. These are 3.0 and 1.6 for K^+ and 3.7 and 2.0 for Na^+ in AN and TMS, respectively. In both cases there is a decrease of about 1.5. For Li^+, Spiro assigned a value of 4.4 in AN, but he gave no value for this ion in TMS. The large size of the sulfolane molecule would certainly prohibit more than two solvent molecules from solvating the small lithium ion. Indeed, one might expect that Li^+ is so completely surrounded by the two oxygen atoms of the sulfone group that not more than one TMS molecule can solvate it. This would lead to Li^+ being relatively less solvated in TMS than other alkali metal ions. Additional evidence will be presented for the relatively low degree of solvation for Li^+ in TMS in a later publication. In any case, the combination of a larger degree of solvation of Li^+ in AN and an equal or perhaps lower degree of solvation in TMS, relative to other cations, will result in a large positive value for $\Delta H^\circ_{\mathrm{TMS}\leftarrow\mathrm{AN}}$ for lithium salts in contrast to the negative values observed for salts of the other alkali metals. In conclusion it appears that at least one of these solvents exhibits specific interactions with Li^+ and is unsuitable as a reference solvent. Additional studies on other potentially useful reference solvents will be helpful in determining whether either of these solvents is suitable as a reference solvent.

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