Thermodynamics of Solution for Benzene in Aqueous Tetrabutylammonium Bromide Solutions[1]

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Received May 5, 1970

Abstract: Relative heats of solution of benzene in aqueous tetrabutylammonium bromide solutions up to 5 *m* have been measured calorimetrically at 25°. When combined with the appropriate solubility measurements, a complete thermodynamic analysis of the "salting-in" is produced. The results bear little or no relation either to theories of electrolyte solutions or of salting-in behavior, but are exactly analogous to the behavior of nonpolar solutes in other mixed aqueous binary solutions and exhibit clearly the earmarks of hydrophobic bonding found in many biological systems. Surface tension measurements rule out micelle formation by the salt over this concentration range.

The tetraalkylammonium salts are a class of electrolytes whose aqueous solutions[2] show unusual properties such as high viscosities with large temperature coefficients,[3] long dielectric relaxation time,[4] and high partial molal heat capacities.[5,6] Some of the salts of large tetraalkylammonium ions form polyhedral clathrate hydrates with many waters of crystallization, whose structures have been analyzed by X-ray diffraction.[7]

While the solubility of nonelectrolytes in water is generally reduced by the common inorganic salts, the tetraalkylammonium ones may have an opposite effect.[8–10] As an example, the solubility of liquid benzene in aqueous solutions of some quaternary ammonium bromides has been determined by a number of workers.[9,11–15] From these solubility data, the free energies for transfer of benzene from water to aqueous solutions of tetraalkylammonium bromides can be calculated. Because of the large salting-in effect, it is practical to measure the heats of solution for benzene in these media and refer them to that in water.[16,17] The corresponding entropies of transfer might then be calculated directly from the free energies and enthalpies provided the processes are comparable (see below). Such thermodynamic properties of transfer for benzene from water to a series of tetrabutylammonium bromide solutions (from 0.50 to 5.00 *m*) at 25° are reported here.

Experimental Section

Heats of solution were measured with an adiabatic solution calorimeter[18] modified as follows. (1) An additional hole was made in the Teflon top of the calorimeter so that a cooling well (a thin glass tube sealed at one end) could be suspended from it. Small increments of Dry Ice were dropped into the well to remove the heat of stirring generated during each measurement. (2) The probe of a Hewlett-Packard quartz thermometer (Dymec Model 2801 A) was suspended midway in the calorimeter so as to monitor the absolute temperature in order that it might be maintained at 25.000 ± 0.002°. The small temperature changes (*ca.* 10^{-2} °) from which ΔH_s was calculated were measured as before with a VECO No. 32A1 thermistor (resistance of 2000 ohms ±20% at 25°).

A gas-tight 500-μl. Hamilton syringe, with Chaney adaptor and a short (~1 in.) small bore (No. 27 gauge) needle, and a pair of stainless-steel stops were used to deliver increments of benzene into the calorimeter.[19] Nine to twelve successive increments (~100 μl. each) were made into each solution (185 ± 2 ml) of Bu_4NBr in order to detect and correct for solute–solute interactions.

Benzene (Baker Analyzed reagent) was dried over CaH_2 and distilled through a helix-packed column. Its purity was confirmed by gas chromatography and refractive index measurements.

Tetrabutylammonium bromide (Eastman Organic White Label) was recrystallized repeatedly and checked for purity by potentiometric titration of the Br^- ion with standard silver nitrate using a silver indicator electrode and a glass electrode as reference. Solutions of known molality with respect to Bu_4NBr were prepared by weighing the proper amount of salts and of distilled, deionized water.

Surface tensions were determined at 26 ± 1° by the duNoüy ring method utilizing a recording tensiometer.[20] The corrections of Harkins and Jordan[21] were applied.

Results

$\Delta \bar{H}_s^\circ$ values were obtained by extrapolation to infinite dilution on a plot of the molar heats of solution resulting from each increment of benzene *vs.* the total molarity of benzene in the calorimeter after addition of that increment (Figure 1). Straight lines were fitted to the 9–12 points obtained from each solution by the least-squares method and the intercept at 0 *M* benzene is $\Delta \bar{H}_s^\circ$. These are presented with their standard deviations in Table I.

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(1) This work was supported by a grant from the Office of Saline Water, United States Department of the Interior.

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Table I. Solubility and Enthalpy Data for Transfer of Liquid Benzene into Aqueous Solutions of Tetrabutylammonium Bromide at 25°

[Bu$_4$NBr]		Benzene solubility[a,b]		$\Delta\bar{H}_s°$,
m	Mole fraction	*m*	Mole fraction	kcal/mol
0.00	0.0000	0.0231 ± 0.003[c]	0.00042 ± 0.00004	0.560,[d] 0.192[e]
0.50	0.0089	0.0533 ± 0.005	0.00095 ± 0.00009	2.382 ± 0.043
1.00	0.0177	0.064 ± 0.008	0.00148 ± 0.00015	3.866 ± 0.051
1.40	0.0246	0.183 ± 0.018	0.0032 ± 0.0003	3.989 ± 0.032
1.70	0.0297	0.305 ± 0.031	0.0053 ± 0.0005	3.464 ± 0.065
2.00	0.0348	0.478 ± 0.048	0.00824 ± 0.00083	3.093 ± 0.038
3.00	0.0513	1.212 ± 0.121	0.0202 ± 0.0021	1.946 ± 0.018
4.00	0.0672	2.46 ± 0.246	0.0397 ± 0.0041	1.243 ± 0.024
5.00	0.0826	3.58 ± 0.358	0.0559 ± 0.0059	1.045 ± 0.018

[a] Solubility of liquid benzene in aqueous Bu$_4$NBr solutions. [b] Interpolated graphically from Professor H. E. Wirth's data, ref 12. We are most grateful to Professor Wirth for supplying some of the data as a personal communication. [c] From ref 11. [d] From ref 16. [e] From ref 17. This is a very recent value measured by direct calorimetry.

It is clear from Figure 1 that measurable benzene–benzene interactions are found in all of the salt solutions; that is to say, the molar heat of solution of this solute depends on the amount of benzene in the solution as well as the concentration of tetrabutylammonium bromide. Furthermore, the slopes of the lines in Figure 1 correlate rather well with the slope of the curve of $\Delta\bar{H}_s°$ *vs.* salt concentration shown in Figure 2. If we consider that the benzene molecules already in solution have the same qualitative effect as tetrabutylammonium ions on the addition of a further small increment of benzene, Figure 2 requires that at low salt concentration the presence of 20 or 30 mmol of benzene makes the addition of further increments of this solute more endothermic. At higher concentrations of salt (past the height of the maximum in Figure 2), the addition of more organic material makes the molar heat of solution of benzene more exothermic. Thus, there is a phenomenological consistency between Figures 1 and 2 if we consider that there is similarity between the way benzene interacts with itself and the way it interacts with this salt.

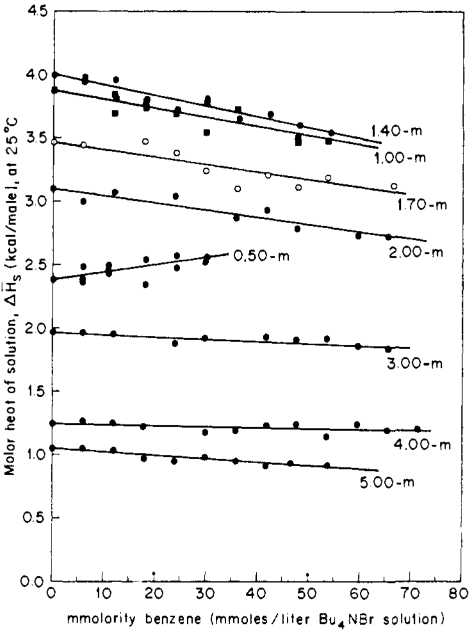

Figure 1. Effect of benzene concentration on its molar heat of solution in a series of aqueous tetrabutylammonium bromide solutions.

The relative thermodynamic quantities of transfer shown in Table II are derived with two assumptions: first, that Franks'[17] new heat of solution for benzene in water is correct; and secondly, that self-interaction free energy terms for benzene are negligible.

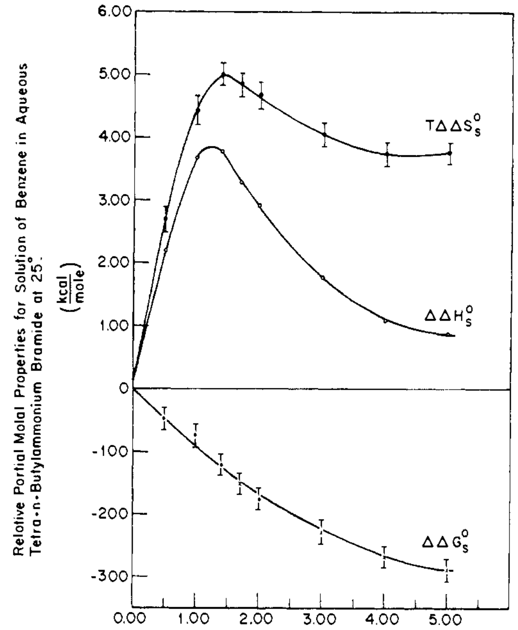

Figure 2. Relative thermodynamic properties of solution for benzene in aqueous tetrabutylammonium bromide solutions (assuming that solute–solute interactions on $\Delta\Delta G_s°$ are negligible).

Discussion

The present study was undertaken in the hope of providing a complete thermodynamic analysis of the salting-in phenomenon for this system. However, the solute–solute (*i.e.*, self-interaction[15]) effects in $\Delta\bar{H}_s$ which are clearly manifested in Figure 1 indicate that our enthalpy data may not be combined rigorously with those free energies of other workers,[12,13] which were obtained at limiting solubility. We believe that the self-interaction effects on $\Delta G°$ will be small for benzene in these media for two reasons. Firstly, the magnitude of the self-interaction term in systems like this[15] appears to be related to the acid–base properties of the solute and benzene is neutral. Secondly, it has been generally observed by ourselves[18] and many others that medium effects in aqueous binaries have a

Table II. Relative Thermodynamic Properties at 25° for Transfer of Benzene from Water to Various Aqueous Solutions of Tetrabutylammonium Bromide[a]

Molality of aqueous solutions of Bu_4NBr	$\Delta\Delta\bar{H}_s°$,[b] kcal/mol	$T\Delta\Delta\bar{S}_s°$, kcal/mol	$\Delta\Delta\bar{G}_s°$, kcal/mol
0.00	0.000	0.000	0.000
0.50	2.190 ± 0.043	2.674 ± 0.205	−0.484 ± 0.162
1.00	3.674 ± 0.051	4.420 ± 0.222	−0.746 ± 0.171
1.40	3.797 ± 0.032	5.000 ± 0.192	−1.203 ± 0.160
1.70	3.272 ± 0.065	4.774 ± 0.226	−1.502 ± 0.161
2.00	2.901 ± 0.038	4.665 ± 0.208	−1.764 ± 0.170
3.00	1.754 ± 0.018	4.052 ± 0.192	−2.298 ± 0.174
4.00	1.051 ± 0.024	3.746 ± 0.197	−2.695 ± 0.173
5.00	0.853 ± 0.018	3.751 ± 0.194	−2.898 ± 0.176

[a] Values of $T\Delta\Delta\bar{S}_s°$ and $\Delta\Delta\bar{G}_s°$ assume that self-interaction terms in $\Delta G°$ are negligible; see text. [b] These values are referred to 0.192 kcal/mol for the reference state in pure water.[17]

much smaller effect on free energy terms than they do on enthalpies or entropies. Since the self-interaction effect on $\Delta\bar{H}_s$ is modest for most of the systems shown in Figure 1, we expect that it will be negligible for the corresponding free energies. This assumption affects all of the free energies and entropies reported here. Its validity could be tested, and corrected, by determining Henry's law constants for benzene over these media. We expect that tetrabutylammonium bromide would have undesirable solubilizing properties which would compromise attempts to use solvent–solvent distribution to determine the self-interaction term.[15] In the absence of Henry's law data, we shall assume in the following commentary that self-interaction free energy terms are small enough to ignore for qualitative discussion.

The data presented here are expressed most effectively in Figure 2, where the relative thermodynamic properties for solution of benzene in the aqueous salt solutions are referred directly to a reference state in water. The salting-out behavior of benzene by various inorganic salts has been studied extensively and is reported by McDevit and Long in their review article.[8] Their attempt to develop a rationale for salting-out phenomena has been discussed in a more recent review[22] by Conway, Desnoyers, and Smith, who propose a somewhat different theory, particularly aimed to include the behavior of polyions. Neither approach is wholly satisfactory for dealing with the salting-out phenomena by simple ions. Bockris and coworkers[23] have considered the salting-in effect, taking particular note of the role of dispersion forces between organic ions and nonpolar solutes. None of these theories may be applied directly to calculations of the free energy changes (solubility) in the present case nor may they be extended to the entropy or enthalpy terms.

Lacking theoretical interpretations, one might consider experimental precedent, but again there are few, if any, published accounts of a complete thermodynamic analysis of salting phenomena to which we may turn. Unpublished results in this laboratory of the enthalpies and entropies of salting out by simple inorganic ions present an entirely different pattern from that shown in Figure 2. Burke[19] has found that the free energy of salting out for a number of nonelectrolytes by simple inorganic salts is dominated by an endothermic trend in the enthalpy at nearly constant entropy. In contrast, the striking feature of Figure 2 is that the increased solubility (exhibited by an increasingly negative free energy of solution) occurs *in spite of* a rapidly increasing endothermic trend in the heat of solution. Figure 2 shows clearly that up to 1.5 *m* salt concentration, the salting in of benzene is entirely the result of a favorable trend in entropy operating in opposition to an unfavorable trend in the enthalpy. Following this, at about 1.5 *m*, both properties undergo a sharp reversal while the free energy of solution continues in a more spontaneous direction as their resultant.

We are unable to interpret the dramatic and partially compensating reversals in $\Delta H°$ and $T\Delta S°$ in terms of present theories of electrolyte solutions or of ordinary binary mixtures. However, the reversals find an exact parallel in the widely observed behavior[2,18,24] of many properties of molecules, ions, and transition states in aqueous binary solutions where the second component is a nonelectrolyte and not a salt. In this sense, the tetrabutylammonium bromide is exhibiting exactly the same enthalpy behavior found previously for *tert*-butyl alcohol and a number of other readily miscible nonelectrolytes. We predict without hesitation that a similar, but not superimposable, result would have been observed had we been using, for example, tributylamine instead of the tetraalkylammonium salt. From previous experience, we propose, therefore, that the charges on the tetrabutylammonium ions are unrelated to the general trend for the thermodynamic properties in the present case.

Desnoyers[11] and Wirth[12] have both suggested that the rapid increase in solubility of benzene as a function of the concentration of tetrabutylammonium bromide could be due to micelle formation in the latter. Lindenbaum and Boyd[25] have cited unpublished measurements which indicate that the critical micelle concentration for tetrabutylammonium bromide lies in the neighborhood of 0.04 *m*. If this were so, the cations must exist primarily in the micellar state over the range of our experiments. However, in view of the close similarity between the behavior of tetrabutylammonium bromide as a "cosolvent" and that of simple nonmicellar cosolvents in water, it seemed unlikely to us that the present phenomena were primarily dependent on the influence of micelles. Accordingly, we determined the surface tension at 25° over the concentration

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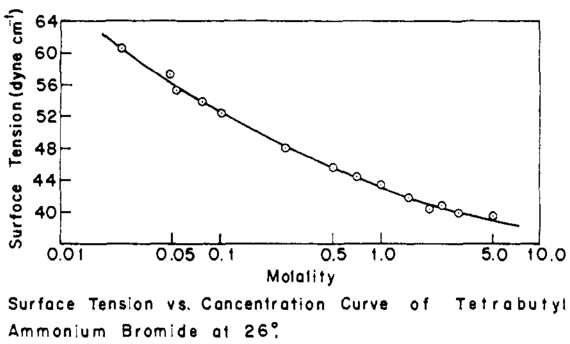

Figure 3. Test for a "critical micelle concentration" of tetrabutylammonium bromide in water at 25°.

range of our experiment. The results are displayed in Figure 3, from which no sharp break such as would suggest a critical micelle concentration can be found. That none is observed at lower concentrations was shown by a similar study of Tamaki's.[26]

The behavior of the thermodynamic properties for solution of benzene in the less concentrated solutions of tetrabutylammonium bromide provides a clear example of "hydrophobic bonding" [27,28] in a very simple system. The results over that part of the curve can be accommodated readily if one considers that the thermodynamics are dominated by the release of water molecules due to aggregation of the benzene with the hydrophobic alkyl chains of the salt. The release of bound water is an endothermic process accompanied by a favorable gain in entropy. This would be true regardless of the nature of the interaction between the water and the hydrophobic chains, and we will make no further attempt to specify the mechanism through which it takes place.

One of the most interesting features of Figure 2 is the sharp reversal in enthalpy and entropy taking place at 1.2 m salt. Reversals of this type have been documented for many processes (see above), and for cases where data are available, it has been found close to the composition of hydrate–clathrates of the cosolvent. The clathrate–hydrate composition of tetrabutylammonium bromide (32.6 to 1[7]) corresponds to a 1.70 m tetrabutylammonium bromide solution, the melting point of the clathrate being 12.5°. The composition and stability of the crystalline clathrate–hydrate must depend upon geometrical lattice forces which are absent in solution. Although we maintain a skeptical attitude toward the existence of clathrates in solution,[6,29] we note that the phenomena portrayed in Figure 2 could be explained completely if there were a competition between benzene and the tetrabutylammonium bromide for structuring of water. Exothermic structure making by benzene should be most successful in the absence of any competitor, that is in pure water. From pure water to a composition in the neighborhood of the clathrate, structure making by benzene would become increasingly difficult (endothermic). After the clathrate stoichiometry of the tetraalkylammonium salt had been satisfied, structure making of water around the benzene molecule could then proceed in the direction of decreasing entropy and exothermic enthalpy. We are uncomfortable with this facile interpretation, but feel compelled to draw attention to it since it fits the facts.

In conclusion, we wish to emphasize the sharp difference between tetrabutylammonium bromide and mineral uniunivalent salts in aqueous solution and the close similarity of it to nonpolar cosolvents. In the present instance, the phenomena have a closer resemblance to "hydrophobic bonding" than to classical salting-in or salting-out phenomena.

Acknowledgment. We are grateful to Mr. Dimitrous Giannakidis for performing a number of the surface tension measurements.

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Singlet Oxygen in the Environmental Sciences. IX.[1] Product Distribution from Reactions of Singlet Molecular Oxygen in the Gas Phase

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Received December 31, 1969

Abstract: The product distribution for the reactions of $O_2(^1\Delta_g)$ with various olefins in the gas phase was determined and compared with those for the liquid-phase dye-sensitized process. The absence of a free-radical autoxidation mechanism in reactions in the gas phase was also noted.

Dye-sensitized photooxygenations of olefins and polynuclear aromatic hydrocarbons have been studied extensively.[3-6] Additional research into the generation of singlet oxygen by the reaction of hydrogen peroxide and sodium hypochlorite has shown that this

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