of relatively low DVB content can be correlated with the transfer of water between the resin and the external aqueous phase. The effect of the halide ions on the structuring of the solvent water in the resin phase must be an important factor in determining the water content of the resin. The similarity in the chemical shifts for the resin halides and tetraalkylammonium halide solutions provides additional support for the view that the observed thermodynamic parameters for anion exchange are not attributable to any specific mode of interaction of the anions within the resin phase.

Phenomenologically, the relationship between the swelling volume of resins and the types of counterions present has been related to the hydration volumes of the ions.[9] As we noted in the introduction, selectivity has been ascribed to the difference in the hydration tendency of the ions exchanging in the external aqueous solution phase[2,7] and in the resin phase.[3] The data in this paper relate selectivity to the differences in hydration in the resin phase as ions are exchanged. From a knowledge of the water content of the pure resin salts for a resin of low DVB, we can predict the values of the selectivity constant and the enthalpy and entropy of exchange for resins of different cross linkages with the values $\Delta G/n_w/\%$ DVB, etc.

We recognize that ion exchange is a very complex phenomenon and selectivity is unlikely to be explained by any single, simple correlation. However, the relative hydration tendencies of the ions must be one of the factors in selectivity. A possible explanation for the relative order of hydration of the pure resin salts has been suggested by Steigman and Dobrow.[10] These authors proposed that "anion selectivities on ion-exchange resins in water are strongly influenced by antagonistic and cooperative interactions of two water atmospheres: that surrounding the quaternary ammonium ion of the resin and that surrounding the entering anion." Qualitatively, such a concept correlates with the greater hydration of RF compared to RCl, etc. For systems of low water content (*e.g.*, resins of higher DVB), it is unlikely that the resinate and the counterion form full hydration spheres and other factors must play dominant roles in selectivity.

Acknowledgments. This research was supported by Contract 14-01-0001-2104 of the Office of Saline Water, Department of the Interior. The NSF also provided some assistance through a grant to the FSU Computer Center.

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(9) F. Helfferich, "Ion Exchange," McGraw-Hill, New York, N. Y., 1962.

(10) J. Steigman and J. Dobrow, *J. Phys. Chem.*, **72**, 3424 (1968).

Thermodynamic Properties of Hydrated and Ammoniated Electrons

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We have found fair agreement between the free enthalpies of solvated electrons as computed from experimental data and from theoretical models. The apparent anomalies in the entropy of the ammoniated electron are due to a looser packing in the first solvation layer relative to the pure solvent, this effect being larger at a lower temperature. Some spectroscopic results can be rationalized in terms of the thermodynamic data.

Introduction

Various thermodynamic properties have been previously computed for hydrated and ammoniated electrons on the basis of experimental data.[1-4] We wish to use these data for a comparative study of the hydrated and the ammoniated electron and for a comparison between the thermodynamic properties of solvated electrons in polar liquids and the results of recent theoretical estimates.[5] To achieve this goal, we require a unified choice of definitions and extra-

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(1) R. M. Noyes, *J. Amer. Chem. Soc.*, **86**, 971 (1964).

(2) J. Jortner and R. M. Noyes, *J. Phys. Chem.*, **70**, 770 (1966).

(3) W. L. Jolly, *Advan. Chem. Ser.*, **No. 50**, 30 (1969).

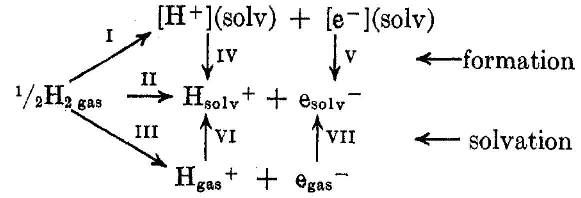
(4) G. Lepoutre and A. Demortier, to be published in *Ber. Bunsenges. Phys. Chem.*

(5) D. A. Copeland, N. R. Kestner, and J. Jortner, *J. Chem. Phys.*, **53**, 1189 (1970).

thermodynamic assumptions for the hydrated and for the ammoniated electron.

Definitions

Let us consider the following set of reactions



Let $X°$ be any standard thermodynamic property ($S, H, G\ldots.$) and $\Delta X°_n$ be its variation during reaction n (n = I, II....).

Let $[H^+]$(solv) and $[e^-]$(solv) be protons and electrons in the solvent in hypothetical states where their $X°$ values and the corresponding $\Delta X°$ values of formation are zero.

Then, we assert that (a) all $\Delta X_I°$ are zero by definition; (b) the values of $\Delta X°_{IV}$ and of $\Delta X°_V$ are individual properties of "formation" of the solvated proton or the solvated electron ($\Delta X°_{IV} = \Delta X_f°_{H_{solv}^+}$; $\Delta X°_V = \Delta X_f°_{e_{solv}^-}$); (c) the values of $\Delta X°_{VI}$ and of $\Delta X°_{VII}$ represent individual properties of "solvation" of the gaseous proton or the gaseous electron.

Extrathermodynamic Assumptions

A. The $\Delta X_f°$ of formation of individual solvated ionic species and their individual standard entropies $S°$ can be separated by reliable extrapolations schemes which involve experimental data concerning a large number of cations and anions. This assumption is quite reliable and is not expected to lead to large errors. Such a method previously applied by Jortner and Noyes to hydrated electrons[1,2] will now be extended to ammoniated electrons. In the case of ammonia, Jolly[3] and Lepoutre[4] had indeed used individual standard entropies, but their $\Delta X_f°$ values of formation were computed on the basis of arbitrary assumption that all the $\Delta X_f°$ values of formation of the ammoniated proton are equal to zero.

B. The $\Delta X_f°$ values of formation of the gaseous electron are equal to their $X°$ values, *i.e.*, $\Delta X_f°_{e_g^-} = X°_{e_g^-}$. As a consequence, for reaction III, we have

$$\Delta X_f°_{H_g^+} = X°_{H_g^+} - {}^1/_2 X°_{H_{2g}}$$

resulting in an asymmetry in the $\Delta X_f°$ values for the proton and for the electron. This asymmetry will forbid us to compare the properties of the solvated proton with the properties of the solvated electron, but we shall still be able to compare the various thermodynamic properties of the solvated electron in different solvents.

C. The $X°$ values for the gaseous electron can be computed as for a perfect gas with translation and spin, providing a "best guess" for these quantities. Jortner and Noyes[2] have applied assumptions b and c for the hydrated electron; we shall apply them here for the thermodynamic properties of the ammoniated electron.

Data

We choose the hypothetical ideal standard molal state for the solvated protons and electrons, and the standard state where the fugacity is 1 atm for the gaseous protons and electrons. We use the results of Jortner and Noyes[2] for the hydrated electron and the results of Lepoutre and Demortier[4] for the ammoniated electron. Some details about our computations are given in Appendix I. We obtain the thermodynamic quantities listed in Table I. For each thermodynamic quantity, we have indicated whether assumptions a, b, and (or) c were used.

Discussion

A. Comments on the Formation of the Solvated Electron. Focusing attention mainly on the features of reactions II, V, and VII, we see from Table I that, although assumption c has not been invoked for the same properties in water and in ammonia, the values obtained in these two solvents are of comparable magnitude. Let us recall that assumption a is safe, that b bears the only inconvenience of forbidding a comparison between protons and electrons, and that assumption c provides a best guess. Looking more specifically at reaction V (the formation of the solvated electron) we find that the standard free enthalpy of formation of the solvated electron is lower in water than in ammonia and that it decreases with increasing temperature in ammonia; this temperature coefficient can be commented in two different ways.

The temperature coefficient of $\Delta G_f°_{e_{am}^-}$ is due to the large decrease of $H_f°_{e_{am}^-}$ with increasing temperature, this effect being only partially compensated by the increase of $(-T\Delta S_f°_{e_{am}^-})$. It may be useful to bear in mind that the enthalpies and the entropies of formation contribute with opposite signs to the temperature coefficient of the free enthalpy of formation. It may also be useful to remember that the large temperature coefficients of $\Delta H_f°_{e_{am}^-}$ and of $\Delta S_f°_{e_{am}^-}$ arise essentially from the experimental reaction II, and that the experimental data yield a small temperature coefficient of $\Delta G°_{II}$ and a large negative temperature coefficient of $\Delta H°_{II}$. Further insight into the nature of the temperature coefficient of $\Delta G_f°_{e_{am}^-}$ is based on the following consideration. Both $-(\partial G°_{e_{am}^-}/\partial_T)$ and $-(\partial G_f°_{e_{am}^-}/\partial_T)$ are equal to $S°_{e_{am}^-}$, the standard entropy of the ammoniated electron. The large positive value of $S°_{e_{am}^-}$ gives rise to the negative temperature coefficient of $\Delta G_f°_{e_{am}^-}$. It should be noted that the value of $S°_{e_{am}^-}$ derived from $G°_{II}$ and from $H°_{II}$ without invoking assumptions b and c.

We thus conclude that the enthalpy of formation of the solvated electron is lower in water than in ammonia

Table I: Thermodynamic Data for Some Reactions Involving the Solvated Electron[a]

		NH_3, −35°	NH_3, +25°	H_2O, +25°
II	$\Delta G°$	+43.7	+44.4	+66.3
	$\Delta H°$	+42.2	+37.4	+62.2 c
	$\Delta S°$	−6.2	−24.2	−13.7 c
IV (H^+)	$\Delta G_f°$	+68.6 a, b, c	+71.1 a, b, c	+103.8 a
	$\Delta H_f°$	+58.3 a, b, c	+58.9 a, b, c	+98.8 a, b
	$\Delta S_f°$	−42.8 a, b	−40.6 a, b	−16.8 a, b
	$S°_{H_{solv}^+}$	−28.0 a	−25.0 a	−1.2 a
V (e^-)	$\Delta G_f°$, $G°$	−24.9 a, b, c	−26.4 a, b, c	−37.5 a, b
	$\Delta H_f°$, $H°$	−16.1 a, b, c	−21.5 a, b, c	−36.6 a, b, c
	$\Delta S_f°$	+36.6 a, b	+16.4 a, b	+3.1 a, b, c
	$S°_{e_{solv}^-}$	+36.6 a	+16.4 a	+3.1 a, c
VII (e^-)	$\Delta G°_{solv}$	−25.1 a, c	−26.4 a, c	−37.5 a, b
	$\Delta H°_{solv}$	−17.3 a	−23.0 a	−38.1 a, b
	$\Delta S_{solv}°$	+32.4 a, c	+11.4 a, c	−1.9 a
III	$\Delta H°$	+366.5	+367.1	+367.1
VI (H^+)	$\Delta H°_{solv}$	−300.3 a	−306.7 a	−266.8 a, b, c
	$S°_{e_{gas}^-}$	+4.2 c	+5.0 c	+5.0 c
	$H°_{e_{gas}^-}$	+1.2 c	+1.5 c	+1.5 c
	$S°_{1/2\ H_2\ gas}$			

[a] All $G°$, $H°$, $\Delta G°$, $\Delta H°$ are in kcal/mol. All $S°$, $\Delta S°$, are in cal/(mol deg).

and is mainly responsible for the lower value of the free enthalpy of formation in liquid ammonia. The standard entropy is also lower in water than in ammonia. It was shown elsewhere[4] that the values of $S°_{e^-}$ in ammonia are exceptionally high. The low positive value of $S°_{e_{ag}^-}$ would yield a very small negative temperature coefficient for $\Delta G_f°_{e_{ag}^-}$.

B. Comparison with Theoretical Values. In a recent paper, Copeland, Kestner, and Jortner (CKJ)[5] have computed the energies of solvated electrons. They state that the total energy, E_t, is the sum of the electronic energy, E_e, and of the medium rearrangement of energy E_M.

$$E_t = E_e + E_M \tag{1}$$

They compute these energies as functions of a configurational variable (the radius R of the cavity) and establish the configuration stability by the conditions

$$(\partial E_t/\partial R)_{R=R_0} = 0; \ (\partial^2 E_t/\partial R^2)_{R=R_0} > 0 \tag{2}$$

Their model accounts for the coordination number N of solvent molecules in the first shell around the electron, and a continuous dielectronic medium beyond this layer. The following comments should be made at this point. (a) E_t is a free enthalpy of the rearrangement of the medium at constant temperature and pressure. The term E_M in eq 1 is the contribution to internal energy of electrostatic interactions involving the solvent molecule. It does not include heat and work contributions to the internal energy. Therefore

$$E_M = H_M = G_M \tag{3}$$

and the total internal energy of rearrangement is

$$E_{Mt} = TS_M - PV_M + E_M \tag{4}$$

Since there are no TS or PV terms in the electronic part of the internal energy, the total internal energy is

$$E_t = E_e + E_{Mt} = E_{el} + TS_M - PV_M + E_M \tag{5}$$

The total free enthalpy is

$$G_t = E_t - TS_M + PV_M = E_{el} + E_M = E_t \tag{6}$$

Therefore, as we have stated, E_t is the total free enthalpy, G_t, of the solvated electron.

(b) We see that condition 2 for configurational stability is correct, since we have to write, at constant T and P

$$(\partial G_t/\partial R)_{R=R_0} = 0 \tag{7}$$

(c) Finally, let us state that in eq 4, 5, and 6, the term PV_M is negligible at ordinary pressures, so that

$$E_{Mt} = H_{Mt} \qquad E_t = H_t \tag{8}$$

We can now proceed to compare theory and experiment. We take the theoretical values of $G_t = E_t$ in the CKJ paper. Equilibrium values in ammonia were given at 203 and 300°K; we interpolate them at 240°K. With CKJ, we have to make assumptions for the appropriate choice of V_0, the electronic energy of the quasi free electron state, and of N, the coordination number. We make the reasonable asumptions that $V_0 = 0.5$ or 0.0 eV and $N = 4$ or 6. For water, instead of having an equilibrium value, we add the assumption that $R_0 = 0.5$ Å.

In Table II, we list these theoretical results for the total free enthalpies of the species $e^-(NH_3)_N$ and $e^-(H_2O)_N$ in a polarizable continuum. These species are formed according to reactions of the type

$$e^-(\text{solv}) + N \cdot NH_3 \longrightarrow e^-(NH_3)_N$$

where $(e^-)(\text{solv})$ is the electron in the hypothetical state with zero free enthalpy and zero free enthalpy of formation.

Table II: Theoretical and Experimental Values[a] for G_T

$$G_T = E_t = \Delta G_f{}^\circ{}_{e_{solv}^-} - 2N/3\Delta G_{vap}{}^\circ$$

Theory (G_T)		NH₃ −35°	NH₃ +25°	H₂O +25°
$V_0 = 0.5$	$N = 4$	*−1.03*	*−0.99*	−1.41
	$N = 6$	−0.93	−0.89	−0.87
$V_0 = 0.0$	$N = 4$	−1.41	−1.37	*−1.91*
	$N = 6$	−1.24	−1.21	−1.23
Experiment				
$\Delta G_f{}^\circ{}_{e_{solv}^-}$		−1.08	−1.15	−1.63
$-{}^2/_3\Delta G_{vap}{}^\circ$		0.00	+0.04	−0.06
$\Delta G_f{}^\circ{}_{e_{solv}^-} - 2N/3\Delta G_{vap}{}^\circ$				
$N = 4$		*−1.08*	*−0.99*	*−1.87*
$N = 6$		−1.08	−0.91	−1.99

[a] All data are in eV.

The theoretical value of G_t and the experimental value of $\Delta G_f{}^\circ{}_{e_{solv}^-}$ cannot be directly compared, as the latter value includes *all* the free enthalpy contributions required to form the electron localization center, while G_t in the CKJ model did not account for all the structural changes required to bring N molecules from the bulk to create the first coordination layer. We shall therefore set

$$G_f{}^\circ{}_{e_{solv}^-} = G_t - N\Delta G_L{}^\circ$$

where $\Delta G_L{}^\circ$ is the difference in the molal free enthalpy (due to attractive intermolecular interactions) between a molecule in the bulk of the pure liquid and in the first coordination layer. A crude estimate of this energy term may be obtained as follows. Apart from lateral interactions, included in G_t, these N molecules may still interact, in the direction of R, with neighbor solvent molecules in the outer shells. We should therefore include in $\Delta G_L{}^\circ$ only about two-thirds of the intermolecular interactions in the pure liquid (or, alternatively, add one-third of this interaction term to G_t). Finally, since we can identify these intermolecular interactions with the cohesion in the liquid state, we set

$$\Delta G_L{}^\circ - {}^2/_3\Delta G^\circ$$

where $G_V{}^\circ$ is the free enthalpy of vaporization, and therefore state that $G_T(\text{theor}) = (\Delta G_f{}^\circ{}_{e_{solv}^-} - {}^2/_3 N\Delta G_V{}^\circ)$ (exptl).

We list the pertinent data in Table II. Let us make the reasonable assumptions[5] that $V_0 = 0.5$ in ammonia and $V_0 = 0.0$ in water. If we choose $N = 4$ for both solvents, the agreement between theory and experiment is fairly good for the absolute values of G_t in different solvents and for the temperature effect. The agreement in respect to the sign of the temperature coefficient dG_t/dT is due to the large positive temperature coefficient of $-\Delta G_V{}^\circ$ which, multiplied by $2N/3$ overwhelms the negative temperature coefficient of $\Delta G^\circ{}_{e_{am}^-}$. Further discussion should concern comparison between theoretical and experimental enthalpies and entropies. Unfortunately, direct theoretical computations of enthalpies or entropies are not presently available.

The present data for the temperature coefficient of G_t in ammonia clearly indicates that the negative temperature coefficient of $\Delta G_f{}^\circ{}_{e_{am}^-}$ and the corresponding positive values of $S^\circ{}_{e_{am}^-}$ are mostly due to what happens to solvent molecules when they are transferred from the bulk of the solvent to the first solvation layer. The new solvent arrangement in the first coordination layer is looser than in the bulk, so that the molecules in the first solvation layer have a larger number of degrees of freedom than in the bulk. It thus seems reasonable that $S^\circ{}_{e^-}$ should be smaller in ammonia at higher temperature, when there is already more freedom in the bulk and still be smaller in water, where the first conduction shell is more tightly solvated.

The present thermochemical data presented herein may be useful to elucidate some of the peculiarities concerning the shape of the optical absorption spectrum of very dilute metal ammonia solutions. The two amazing features of the optical spectrum are (a) a pronounced asymmetry on the high energy side, (b) the half-line width is practically temperature independent.[6,7] The theoretical calculations[5] of the line shape for a constant N predict a practically symmetric line shape for the $1s \rightarrow 2p$ transition where the half-width should reveal a temperature dependence proportional to $T^{1/2}$. The pronounced experimentally observed asymmetry can be rationalized by invoking higher bound and bound and bound-continuum transitions; however, still the half-line width (or the second moment of the intensity distribution) should be temperature dependent. One has therefore to invoke the idea of a compound line shape where electron cavities characterized by different N values yield a different contribution at different temperatures. The values of $\delta G_t = G_t\ (N = 4) - G_t\ (N = 6)$ are practically temperature independent, being $\delta G_t = 0.10$ eV both at −35 and at +25° (see Table II). Although the absolute value of δG_t is by no means certain, one may conclude that at higher temperatures the contribution of the $N = 6$ clusters will increase, thus leading to an additional source of broadening which increases at higher temperature, in contrast to the experimental spectroscopic data. However, once the contribution of the $\Delta G_L{}^\circ$ term is included we find that the free enthalpy difference $\delta G = \Delta G_f{}^\circ{}_{e_{solv}^-}$ $(N = 4) - \Delta G_f{}^\circ{}_{e_{solv}^-}$ $(N = 6)$ from $\delta G = -0.10$ eV

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(6) R. K. Quinn and J. J. Lagowski, *J. Phys. Chem.*, **73**, 2326 (1969).

(7) S. Golden and T. R. Tuttle, in "Metal-Ammonia Solutions" (Colloque Weyl II, 1969), J. J. Lagowski and M. J. Sienko, Ed., Butterworths, London, 1970.

at 35° to $\delta G = -0.18$ eV at +25° whereupon at higher temperatures the $N = 4$ structure will be favored. Thus at lower temperatures we may expect a substantial contribution to the optical absorption band from both the $N = 4$ and the $N = 6$ species, the compound line shape will narrow with increasing temperature due to the diminished contribution of the $N = 6$ species, while each $N = 4$ and $N = 6$ component suffers phonon broadening so that the resulting line width remains constant. It appears thus that some of the puzzling spectroscopic observations can be adequately rationalized in view of the new thermodynamic data.

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Appendix: Details for Table I

1. Water, 25°.

Reaction IV: Reliable extrapolations[1] yield $\Delta G_f°$ and $S°$. Assumption b gives then $\Delta S_f°$ and $\Delta H_f°$.

Reaction V: Reliable extrapolations[1] and comparisons[2] yield $\Delta G_f°$. Reliable comparisons[2] and assumption c yield $S°$. Assumption b gives then $\Delta S_f°$, $H_f°$ and $G°$ and $H°$.

Reaction II: Sum of IV and V; does not depend on assumptions a and b, which are cancelled; still depends on reliable comparisons used for reaction V.

Reaction VII: Reliable comparisons[2] yield $\Delta S°$. Assumptions c and b, and the data of reaction V, give $\Delta G°$ and $\Delta H°$.

Reaction VI: Assumptions c and b, and the data of reactions IV and III, give $\Delta H°$.

2. Ammonia, +25 and −35°.

Reaction II: Experimental data, no assumption.

Reaction VII: Reliable extrapolations[8] give $\Delta H°$ at 25°. We take the revised value of ref 5. Reliable extrapolations[4] give $S°_{\mathrm{H}^+}$ at +25 and at −35°. The data of reaction II at both temperatures give $S°_{\mathrm{e}^-}$. By writing $T(\mathrm{d}S_{\mathrm{e}^-}/\mathrm{d}T)_\mathrm{p} = (\mathrm{d}H/\mathrm{d}T)_\mathrm{p}$ we obtain the approximate variation of $\Delta H°$ between +25° and −35°. This gives $\Delta H°$ at −35°. From $\Delta H°$, $S°$, and assumption c, we compute $\Delta S°$ and $\Delta G°$ at both temperatures.

Reaction VI: The data of reactions II, III, and VII, give $\Delta H°$.

Reaction V: As already stated, $S°_{\mathrm{e}^-}$ is obtained through reliable extrapolations and the data of reaction II. $\Delta S°$ is then given by assumption b. $\Delta G°$ and $\Delta H°$ are obtained with assumptions b and c and the data of reaction VII.

Reaction IV: Difference between reactions II and V.

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(8) J. Jortner in "Metal Ammonia Solutions," G. Lepoutre and M. J. Sienko, Ed., W. A. Benjamin, New York, N. Y., 1964.