Solvation of Ions. II. Use of a Variable Solvation Number for K^+

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Gibbs free energies of transfer of K(I) ion from water to water-dimethyl sulfoxide mixtures corrected to zero ionic strength have been used to deduce information concerning states of solvation of K^+ ion in the purely aqueous phase and in the mixed solvent phase. It was found that the largest number of water molecules which needed to be assigned to the solvent cage of K^+ was 11 in either phase. The partition equilibrium constant, β_0, for the distribution of $K(H_2O)_{11}^+$ between the two phases was found as a function of the mole fraction of dimethyl sulfoxide in the mixed solvent phase. The largest number of dimethyl sulfoxide molecules which needed to be assigned to the solvent cage was 10. The number of solvent molecules in the solvent cage was allowed to be variable and the overall formation constants of all $K(H_2O)_j((CH_3)_2SO)_k^+$ ions contributing to the free energy of transfer were determined. The results are compared with the results from molecular dynamics computer simulations for K^+ where possible.

An ion in a solvent can be thought of as possessing a solvent »cage« around the central ion which includes all solvent molecules that contribute significantly to the measured values of the physical property being considered and which does not include the distant solvent molecules which interact only by long distance ion-dipole (permanent or induced) forces with the central ion. This solvent cage includes the solvent

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molecules in the primary solvation shell and in the secondary solvation shell(s) if there are such. In the primary solvation shell the solvent molecules are considered to be more or less in direct contact with the central ion (whatever their individual orientations may be) and they do not have other solvent molecules occupying the space between them and the central ion. In the secondary solvent shell(s) the partially oriented solvent molecules have other solvent molecules intrvening between them and the central ion. For any given ion in any given solvent the number of solvent molecules in its solvent cage need not be, and probably is not, a constant number. With passage of time, the number, n_i, of solvent molecules in the solvent cage of the ion may vary between a (theoretically possible) value of zero and some maximum number n. In particular, K^+ ions in a purely aqueous phase at zero ionic strength may be represented by KW_i^+ ($i = 0, 1, \ldots , n$) where W represents a water molecule. Equilibrium between these various states of solvation at constant temperature and pressure may be represented by equation (1) where the bar over the formula means that the species is in purely aqueous medium and where the equilibrium

$$\overline{KW_n^+} \rightleftharpoons \overline{KW_i^+} + (n - i)\,\overline{W} \; ; \quad \gamma_i \tag{1}$$
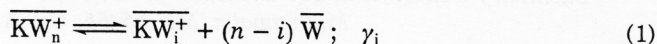
constant, γ_i, for the reaction is given by equation (2). Because the activity of

$$\frac{\overline{[KW_i^+]}\,\overline{a_w^{n-1}}}{\overline{[KW_n^+]}} = \gamma_i , \quad i = 0, 1, \ldots, n \tag{2}$$

water, a_w, in these purely aqueous media at zero ionic strength is equal to unity, the concentrations of the KW_i^+ species are given by equation (3). In equations (2) and (3)

$$\overline{[KW_i^+]} = \gamma_i\,\overline{[KW_n^+]} , \qquad i = 0, 1, \ldots, n \tag{3}$$

when $i = n$, $\gamma_i = 1$ and $\overline{[KW_n^+]} = \overline{[KW_n^+]}$ (of course); in later calculations it is convenient to retain n as the upper limit of i.

## Methodology

Let the purely aqueous phase be connected to the mixed solvent phase with a membrane permeable only to KW_n^+. Potassium ion is transferred from the aqueous to the mixed solvent phase where various solvated ions $KW_jD_k^+$ are formed. (The second component of the mixed solvent is represented by D and is taken to be dimethyl sulfoxide for the quantitative calculations. Water molecules continue to be represented by W.) When equilibrium is re-established, N mol of K(I) has been transferred from aqueous to mixed solvent phase. In the aqueous phase, all KW_i^+ concentrations have changed to new equilibrium values. The change in free energy accompanying the change in the purely aqueous phase is given by:

$$\overline{\Delta G_w} = NRT \frac{\sum_{i=0}^{n} \gamma_i \ln \gamma_i}{\sum_{i=0}^{n} \gamma_i} \qquad (4)$$

and it is a contribution to the free energy of transfer of potassium ion between the two media.

The overall formation constants for the formation of the $KW_jD_k^+$ ions from KW_n^+, as shown in reaction (5), are given in equation (6). All formulas of all ions

$$KW_n^+ + kD \rightleftharpoons KW_jD_k^+ + (n-j)W \qquad (5)$$
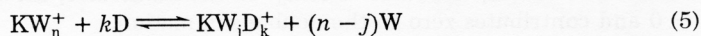
$$\beta_{jk} = \frac{[KW_jD_k^+] \, a_w^{n-j}}{[KW_n^+] \, a_d^k} \qquad (6)$$

and molecules shown without bars above them represent ions and molecules in the mixed solvent. The a_w and a_d are the activities of water and solvent D, respectively, and are known for all mole fractions X_d in the range $0 \leq X_d \leq 1.0$ from excess free energies of mixing water and solvent D.

The equilibrium constant for the distribution of KW_n^+ between the two different phases according to equation (7):

$$\overline{KW_n^+} \rightleftharpoons KW_n^+ \qquad (7)$$

is given by equation (8). This equilibrium constant, unlike the β_{jk}, is dependent on the

$$\beta_0 = \frac{[KW_n^+]}{[\overline{KW_n^+}]} = \exp(bX_d + cX_d^2) \qquad (8)$$

mixed solvent composition because it takes into consideration changes in the long range forces between the central ion and the solvent *outside* the solvent cage as X_d changes.

The β_{jk} for the formation, from KW_n^+, of ions with solvent cage compositions different from that of KW_n^+ concern changes in the composition of the solvent cage; changes in the bulk solvent outside the solvent cage affect a_w and a_d but not the thermodynamic equilibrium constants β_{jk}.

It is readily shown that the free energy change accompanying the establishment of the equilibrium concentrations of $KW_jD_k^+$ ($j = 0, 1, ..., n$; $k = 0, 1, ..., m$) in a mixed solvent of composition X_d is given by equation (9).

$$\Delta G_d = -NRT \left\{ \ln\beta_o + \frac{\displaystyle\sum_{k=0}^{m} \sum_{j=0}^{n} \frac{a_d^k}{a_w^{n-j}} \beta_{jk} \ln \beta_{jk}}{\displaystyle\sum_{k=0}^{m} \sum_{j=0}^{n} \frac{a_d^k}{a_w^{n-j}} \beta_{jk}} \right\} \tag{9}$$

The summations over j and k are independent because we allow for all possibilities that the total number of solvent molecules in the solvation shell may range from zero ($j = 0$, $k = 0$) to a maximum of $(n + m)$ ($j = n$ = maximum number of water molecules ever to appear in the solvent cage; $k = m$ = maximum number of solvent D molecules ever to appear in the solvent cage). When $j = n$ and $k = 0$, the term $(a_d{}^0/a_w{}^0)\beta_{n0}$ in the denominator is equal to unity because β_{n0} represents the formation of $KW_n{}^+$ from $KW_n{}^+$ and has, of course, the value of unity. In the numerator, the term $(a_d{}^0/a_w{}^0)\beta_{n0}\ln\beta_{n0} = 0$ and contributes zero to the double summation.

The total free energy changes for zero ionic strength accompanying the transfer of N mole of K(I) from the purely aqueous phase to the mixed solvent phase of composition X_d is the sum of the free energy changes given in equations (4) and (9). If this sum is divided by N, we will, of course, obtain $\Delta G_t{}^o(K^+)$, the free energy of transfer per mole of K(I) for temperature T and composition X_d. It is convenient to divide the expression for $\Delta G_t{}^o(K^+)$ by $(-RT)$ to give a dimensionless free energy of transfer r_d. Similarly, it is convenient to define the ratio of the summations in equation (4) as a constant a:

$$a = -\sum_{i=0}^{n} \gamma_i \ln \gamma_i \bigg/ \sum_{i=0}^{n} \gamma_i \tag{10}$$

because this ratio is independent of the nature of the mixed solvent. Thus, using equations (8) and (10), we can write for r_d:

$$r_d = a + bX_d + cX_d^2 + \frac{g(n,m,d)}{f(n,m,d)} \tag{11}$$

where

$$g(n,m,d) = \sum_{k=0}^{m} \sum_{j=0}^{n} \frac{a_d^k}{a_w^{n-j}} \beta_{jk} \ln \beta_{jk}$$

and

$$f(n,m,d) = \sum_{k=0}^{m} \sum_{j=0}^{n} \frac{a_d^k}{a_w^{n-j}} \beta_{jk}$$

The experimental values for r_d, a_d and a_w are known for water + dimethyl sulfoxide mixtures over the entire solvent range X_d. The method of least squares was applied to find the values of the unknown parameters (a,b,c and the β_{jk}) which gave the

best fit between calculated (r_{dc}) and experimental (r_{de}) values of r_d. Derivatives of the function:

$$\sigma^2 = \sum_{dp} \left(\frac{r_{dc} - r_{de}}{r_{de}} \right)^2 \tag{12}$$

were taken with respect to each of the unknown parameters to yield as many equations as unknowns. The summation was taken over many more data points (dp) than there were unknowns. The values of the unknowns giving the best fit a given (n,m) pair of values were determined. The (n,m) pair giving the best fit (smallest standard deviation) to the experimental values was deemed to give the best available interpretation of the system.

RESULTS

The percent standard deviation was smallest (9.7892×10^{-4}) for $n = 11$, $m = 10$, and was approximately only two-thirds of that for the next best fit which was: $n = 10$, $m = 10$. For the $n = 11$, $m = 11$ case, the error decreased with decreasing β_{j11} until all $KW_jD_{11}^+$ ions had been eliminated; this results clearly showed that $m = 11$ was not required to interpret the experimental results. Use of $n = 10$ or $n = 12$ led to larger errors and poorer fit. Generally, the use of smaller n and m values, and hence fewer equilibrium constants, led to larger errors.

The value of β_0 is determined by the molar free energy of transfer of the KW_n^+ species from the purely aqueous phase to the mixed solvent phase, $-RT\ln\beta_0$, and is independent of the subsequent equilibria. Furthermore, the contribution made by ΔG_w per mole is small at $X_d > 0.1$. For small ranges of X_d, say, $\Delta X_d = 0.005$ or less, $\ln\beta_0$ can be assumed to be constant so that equation (11) can be written as

$$r_d \cong \ln\beta_0 + g/f$$

and the error function minimized with respect to $\ln\beta_0$ and the β_{jk} for each ΔX_d range. The $\ln\beta_0$ thus found had a quadratic dependence on the mid-range X_d value. The coefficients b and c were not determined in this manner; they were determined in the more rigorous treatment of error over the range $0.05 \leq X_d \leq 0.95$, as described above. The values of b and c for $n = 11$, $m = 10$ were 4.211743 and 8.853950, respectively, giving equation (13) for $\ln\beta_0$ as a function of the mixed solvent composition.

$$\ln \beta_o = 4.211743 X_d + 8.853950 X_d^2 \tag{13}$$

The value of constant a in equation (10) was found to be 0.287533, giving a value of ΔG_w^o equal to -713 J/mol.

Of the β_{jk} defined by equation (6) only those for which experimentally significant amounts of $KW_jD_k^+$ were formed will be reported. The remainder of the β_{jk} were too small to give a contribution to the error; further reduction of their values or small increases in their values had no effect on the error of the fit because the concentrations of the corresponding ionic species were insignificant. For example, $KW_0D_0^+$ and $KW_{11}D_{10}^+$ were not present in experimentally significant amounts and β_{00} and $\beta_{11,10}$ values could not be determined and, therefore, will not be reported.

The significant β_{jk} were as follows:

$\beta_{11,0} = 1$. (Of course, the formation constant for KW_{11}^+ from KW_{11}^+ in the mixed solvent phase is unity; all other solvated ions in the mixed solvent phase are formed from this ion.)

$\beta_{8,1} = 0.0117$

$\beta_{7,1} = 0.6134$

$\beta_{6,2} = 0.1128$

$\beta_{5,3} = 0.2379$

$\beta_{4,4} = 0.4585, \beta_{4,5} = 0.06937$

$\beta_{3,6} = 0.03266, \beta_{3,7} = 0.02143, \beta_{3,8} = 0.4647$

$\beta_{2,6} = 3.287 \times 10^{-4}, \beta_{2,7} = 1.672 \times 10^{-3}, \beta_{2,8} = 2.639 \times 10^{-3}, \beta_{2,9} = 9.828 \times 10^{-5},$
$\quad \beta_{2,10} = 0.02041$

$\beta_{1,7} = 6.783 \times 10^{-4}, \beta_{1,8} = 1.121 \times 10^{-3}, \beta_{1,9} = 2.926 \times 10^{-3}, \beta_{1,10} = 1.332 \times 10^{-3}$

$\beta_{0,8} = 1.346 \times 10^{-3}, \beta_{0,9} = 7.497 \times 10^{-4}, \beta_{0,10} = 1.888 \times 10^{-4}$

It is seen that the smallest number of solvent molecules in the solvent cage is 8 and that the number of water molecules in the solvent cage is quickly reduced by the presence of dimethyl sulfoxide in the bulk phase of the mixed solvent. The dimethyl sulfoxide has a greater affinity for water than the potassium ion and the latter loses water (probably in what might be termed the second solvation shell) which is not replaced mole-for-mole by dimethyl sulfoxide. At $X_D \leq 0.35$, the number of differently solvated ions in solution remains small. At $X_D \simeq 0.45$, the number of differently solvated ions in solution begins to proliferate and, for example, $KW_2D_k^+$ ($k = 6,7,8,9,10$) all exist. It is interesting to note that the ion KD_{11}^+ with a one-to-one replacement of the original 11 molecules of water by dimethyl sulfoxide did not appear; attempts to introduce or retain an ionic species with 11 dimethyl sulfoxide molecules in the solvent cage led to only markedly increased error.

The maximum number of water molecule in the solvent cage of potassium ion in the purely aqueous phase was found to be 11. All attempts to use a larger or smaller number resulted in substantially increased error. This result is in very good agreement with the 11–12 water molecules reported by Malenkov[1] for computer simulations with different water models. The modified Covington[2] model used in a previous study of K^+ solvation[3] gave a larger value of 14 solvent molecules for the solvent cage but it did not allow for variable solvent cage size as this study does.

The solvation number of 8 is an important one. The solvated ions KW_7D^+, $KW_6D_2^+$, $KW_5D_3^+$, $KW_4D_4^+$, $KW_2D_6^+$, KWD_7^+ and KD_8^+ all appear to exist in quantities sufficient to contribute experimentally significant amounts to the free energy of transfer per mole of potassium ion. Again, this result is in good agreement with the value of approximately 7.5 reported by Malenkov[1] for the number of water molecules within a radius of approximately 3.5 Å or within what might be termed the first solvation shell of K^+. When dimethyl sulfoxide is added to the purely aqueous phase, the strong affinity of dimethyl sulfoxide for water, as evidenced by the large exothermic heat of mixing, removes the more loosely held water molecules of the second solvation shell. At $x_D > 0.35$, where there is more than sufficient dimethyl sulfoxide to form the well-known 2:1 water-dimethyl sulfoxide complex, the extra dimethyl sulfoxide molecules start appearing in the solvent cage so that the total number of solvent molecules there becomes greater than 8 and reaches a maximum value of 12 in $KW_2D_{10}^+$.

TABLE I

Comparison of experimental and calculated values of $\Delta G_t^\circ(K^+)$ for transfer of K^+ from purely aqueous to mixed water-dimethyl sulfoxide media and the corresponding percent relative error. 25.00 °C.

$X_d{}^a$	$\Delta G_t^\circ(\text{expt})^b$	$\Delta G_t^\circ(\text{calc})^b$	Percent relative error
0.05	−350	−350	−0.11
0.15	−1665	−1666	+0.05
0.25	−3516	−3512	−0.09
0.35	−5522	−5528	+0.11
0.45	−7411	−7409	−0.03
0.55	−9017	−9013	−0.04
0.65	−10276	−10276	0.00
0.75	−11234	−11245	+0.10
0.85	−12041	−12043	+0.01
0.95	−12953	−12952	−0.01

a) Mole fraction of dimethyl sulfoxide is based on the bulk solvents.
b) J/mol. Values are given to the nearest integral value only to show the agreement between the calculated value and the experimental value obtained as described in the text.

The important solvation number of 8 is also in good agreement with the first-coordination-shell solvation number of 7.8 extending out to 3.52 Å found by Migliore[4] et al. using the ST2 water model, and molecular dynamics computer simulations. The latter authors pointed out their results were in good agreement with the results of previous molecular dynamics computer simulations using different water models and with X-ray data.

Table I shows the experimental and calculated values of $\Delta G_t^\circ(K^+)$ and the percent relative error for selected values of X_d. The experimental values in Table I were obtained using a fourth degree polynomial fit for the experimental data obtained from Cox, Natarajan and Waghorne[5] with $\Delta G_t^\circ(Ph_4As^+)/\Delta G_t(BPh_4) = 1.08$ as recommended by Kim[6]. The coefficients of this polynomial for $\Delta G_t(K^+)$ were: $A_0 = -40.6232132150504$, $A_1 = -3201.80769012073$, $A_2 = -64638.7813651928$, $A_3 = 98401.2596729141$, $A_4 = -44076.9269451916$. The fit of the calculated values with the experimental values is very good. Thus, the derived β_{jk} are capable of giving a very good fit for the free energy of transfer data for K^+ and of giving satisfactory agreement with those results of molecular dynamics (MD) computer simulations where comparison can be made.

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SAŽETAK

Solvatacija iona.II. Upotreba promjenljivog solvatacijskog broja za K⁺.

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Gibbsove slobodne energije prenosa K(I) iz vode u smjese voda-dimetilsulfoksid, korigirane na ionsku jakost nula, upotrebljene su za dobijanje podataka o stanjima solvatacije K^+ iona u čistoj vodenoj fazi i u fazi mješovitog rastvarača. Nađeno je da je najveći broj molekula vode, koji je trebao biti pripisan kavezu rastvarača K^+, iznosio 11 u obje faze. Particijska ravnotežna konstanta, β_0, za raspodjelu $K(H_2O)_{11}^+$ između dvije faze bila je nađena kao funkcija molnog udjela dimetilsulfoksida u fazi mješovitog rastvarača. Najveći broj molekula dimetilsulfoksida, koji je trebao biti pripisan kavezu rastvarača, bio je 10. Varirajući broj molekula rastvarača u kavezu rastvarača određene su ukupne konstante stvaranja, $K(H_2O)_j((CH_3)_2SO)_k^+$, svih iona koji pridonose slobodnoj energiji prenosa. Rezultati su upoređeni, gdje je to bilo moguće, s rezultatima računskih simulacija molekulske dinamike za K^+.