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Solvation of Potassium Ion in Water and in Water-Dimethyl Sulfoxide Mixtures

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A model has been obtained for the solvated K^+ ion in the solvents named in the title using a modified Covington approach. The solvation number in this model was determined to be 14 of which 6 molecules were found to be unique and which were assigned to the inner solvation shell. These 6 inner solvent molecules were unique in that the stepwise formation constants for replacement of water by dimethyl sulfoxide were found to be given by the first stepwise formation constant K_1 , and the statistical factors in the first six stepwise formation constants. The remaining eight solvent molecules were assigned to an outer solvation shell. Their stepwise formation constants for replacement of water by dimethyl sulfoxide were given by K_1 , statistical factors and a power of a parameter k which determines changes in the free energy of the stepwise formation reaction exclusive of contributions from changing statistical factors. The stepwise formation constants (K_0 to K_{14} inclusive) and the free energies of transfer of each of the 15 specie $KW_{14-i}D_i^+$ ($i=0,1,\dots,14$) were used to compare the calculated free energies of transfer of K^+ from water (W) to water (W) — dimethyl sulfoxide (D) mixtures with the experimental values. The agreement was satisfactory.

INTRODUCTION

Many studies¹⁻¹³ have attempted to elucidate the state of solvation of K^+ in solutions. The K^+ ion has been classed as »structure breaking« and to have an effective »negative hydration number« in water solutions.⁶ It has also been assigned solvation numbers ranging from 0.9 in diethylformamide² to 6 octahedrally coordinated water molecules⁷ in purely aqueous solutions. The latter result was obtained from X-ray diffraction study but X-ray diffraction has also given a solvation number of 4.⁸ Using computer simulations for different water structures, Malenkov¹³ reported a first-shell coordination number of approximately 7, evidence of chaotically ordered water molecu-

les between first-coordination-shell water and bulk water, and approximately 12 water molecules within an ion-oxygen radius of approximately 45 nm. Clearly, different physical methods have given different solvation numbers for K^+ and the same physical method has given different solvation numbers in the hands of different investigators. In principle, because of the charge on the K^+ ion and the fact that electrical field decreases only as the inverse of the squared distance from the charge, the K^+ should influence every solvent molecule in the solution. In practice there is a very limited distance over which this influence exerts a significant effect. It would be useful to have a model of the solvated K^+ ion for its own intrinsic interest, for use in the study of K^+ in solutions containing crown ethers and seculchurates and for use in the study of K^+ in biological systems. One way to obtain such a model is to use the available free energies of transfer of potassium iodide from a purely aqueous medium to water + dimethyl sulfoxide mixtures over the entire range of mole fractions of the solvents and the approach of Covington and co-workers¹⁴.

In the approach of Covington three parameters are used to describe solvation of an ion: (1) n , the solvation number of the ion, (2) $x = \beta_n^{1/n}$, the n th root of the overall equilibrium constant for the replacement of n molecules of solvent A by n molecules of solvent B, and (3) k which, in the expression $-RT \ln k$, gives the change in the stepwise free energy of substitution as the substitution progresses exclusive of changes in statistical factors. This approach assumes that n , the solvation number, remains constant throughout the process of replacing solvent A in the solvation shell of the ion by solvent B. The assumption of constant solvation number when dimethyl sulfoxide replaces water in the solvent cage is supported by kinetic results for the $[Co(NH_3)_5H_2O]^{3+} + (CH_3)_2SO \rightleftharpoons [Co(NH_3)_5(CH_3)_2SO]^{3+} + H_2O$ solvent — interchange reaction.¹⁵ The constant solvation number and the compositions of the solvent cage surrounding the inert cobalt(III) complex were used to explain, in a simple, direct manner, the dependency on solvent composition of the first-order rate constants for solvent interchange.

GIBBS FREE ENERGIES OF TRANSFER OF K^+ FROM WATER TO DIMETHYL SULFOXIDE

The data of Cox, Natarajan and Waghorne¹⁶ for free energies of transfer of potassium iodide were used for mol fractions, X_D , of dimethyl sulfoxide, Me_2SO , less than unity. For unit mol fraction of Me_2SO the free energy of transfer of K^+ , $\Delta G_t^0(K^+)$, recommended by Marcus¹⁷ was used. The values of $\Delta G_t^0(K^+)$ are based on the ratio

$$\frac{\Delta G_t^0(Ph_4As^+)}{\Delta G_t^0(BPh_4^-)} = 1.08$$

recommended by Kim,¹⁸ not on $\Delta G_t^0(Ph_4As^+) = \Delta G_t^0(BPh_4^-)$ for the free energies of transfer of the tetraphenylarsonium and tetraphenylborate ions. The $\Delta G_t^0(K^+)$ and X_D values were fitted to a fourth order polynomial so that $\Delta G_t^0(K^+)$ could be conveniently calculated at mol fractions of X_D over the range $0.0 \leq X_D \leq 0.95$ where the activities of water and Me_2SO were

conveniently known from previous studies on preferential solvation.^{15,19} The polynomial obtained is given in eqn (A)

$$\Delta G_{tj}^0(K^+) = a + b X_{Dj} + cX_{Dj}^2 + dX_{Dj}^3 + eX_{Dj}^4 \quad (\text{A})$$

where $a = -104.4781498$, $b = -2237.061251$, $c = -68586.82948$, $d = -104229.09197$ and $e = -46858.44156$ for the units of joule/mol. The plot of $\Delta G_{tj}^0(K^+)$ versus X_D is shown in Figure 1 where the continuous curve is the plot of eqn (A) and the dots are the experimental data points. The fit is most satisfactory.

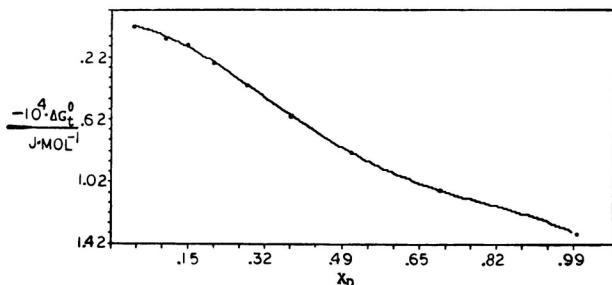
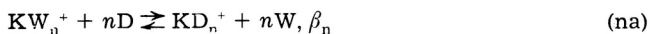
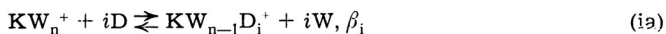
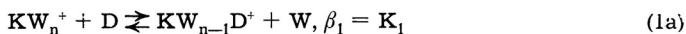
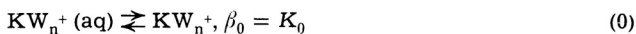


Figure 1. Free energies for transfer of K^+ , ΔG_{tj}^0 , from water to water-dimethyl sulfoxide mixtures versus X_D , the mol fraction of dimethyl sulfoxide.

THE MODEL FOR SOLVATED K^+ ION

The ΔG_{tj}^0 obtained from eqn (A) for 201 X_D values in the range $0.1 \leq X_D \leq 0.9$ were converted to a unitless free energy of transfer G_{tj}^0 by division by $-RT$ for 25.00°C . These G_{tj}^0 were fit by an equation containing the three parameters n, k, x , of the Covington¹⁴ approach to the solvation of ions. The equation relating G_{tj}^0 to n, k and x was derived in the following way.

Consider a purely aqueous solution of potassium ion containing a concentration of C_0 mol dm^{-3} of KW_n^+ (aq) where W represents a water molecule in the solvation sphere which has a total of n water molecules in it. A hypothetical semipermeable membrane, permeable *only* to the KW_n^+ species, separates this solution from a mixed $\text{H}_2\text{O}-\text{Me}_2\text{SO}$ solvent. The KW_n^+ species can move freely through the membrane to the mixed solvent where it can form the $KW_{n-i}D_i^+$ specie ($i = 0, 1, \dots, n$). At equilibrium the following equilibria will exist:



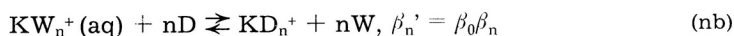
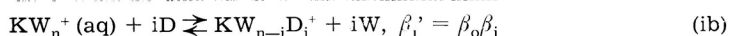
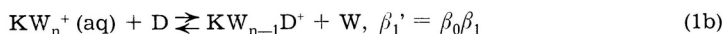
where D represents a dimethyl sulfoxide molecule, W represents a water molecule, the $KW_{n-i}D_i^+$ ($i = 0, 1, \dots, n$) represent $K(\text{I})$ ions in the mixed solvent with varying degrees of replacement of W by D in the solvation sphere of $K(\text{I})$, and the β_i represent the equilibrium constants for the formation of the $KW_{n-i}D_i^+$ ions ($i = 1, \dots, n$) from KW_n^+ in the mixed solvent, not from

KW_n^+ (aq). In particular β_0 is the equilibrium constant for the distribution of the unsubstituted KW_n^+ species between the purely aqueous medium and the mixed solvent medium. It will be different from unity to the extent that interactions between K^+ (with its surrounding solvation sphere) and the solvent outside the solvation sphere are different in the purely aqueous and the mixed solvent media. It is given by the expression

$$\beta_0 = \frac{[\text{KW}_n^+]}{[\text{KW}_n^+ \text{ (aq)}]}$$

because the ΔG_t^0 data have all been corrected to unit activity coefficients using the Davies equation¹⁶.

The equilibria in eqns (1a), (1a) and (na) can be written as:



At equilibrium the total concentration of potassium(I) specie per liter of mixed solvent solution is N mol/liter so that

$$\begin{aligned} N &= [\text{KW}_n^+] + \dots + [\text{KW}_{n-i}\text{D}_i^+] + \dots + [\text{KD}_n^+] \\ &= [\text{KW}_n^+] \left\{ 1 + \sum_{i=1}^n \beta_i y^i \right\} \end{aligned}$$

where y is the ratio of the activities of Me_2SO and water in the solvent mixture of interest and where the activities of the two solvents were calculated as described earlier¹⁹. Thus the equilibrium concentration of KW_n^+ is given by

$$[\text{KW}_n^+] = N \{ 1 + \sum \beta_i y^i \}^{-1} \quad (2)$$

and that of the i th species is given by

$$[\text{KW}_{n-i}\text{D}_i^+] = N \beta_i y^i \{ 1 + \sum \beta_i y^i \}^{-1} \quad (3)$$

At equilibrium $[\text{KW}_n^+]$ mol/liter of potassium(I) has been transferred from the purely aqueous medium to the mixed solvent medium with a standard free energy change per mol of $\Delta G_0^0 = -RT \ln \beta_0$ and an accompanying contribution ΔG_0 to the free energy of transfer given by

$$\Delta G_0 = [\text{KW}_n^+] \Delta G_0^0 = -NRT \ln \beta_0 \{ 1 + \sum \beta_i y^i \}^{-1}$$

Similarly the contribution ΔG_i to the free energy of transfer of $[\text{KW}_{n-i}\text{D}_i^+]$ mol/liter of KW_n^+ (aq) in the purely aqueous medium into $\text{KW}_{n-i}\text{D}_i^+$ in the mixed solvent medium is given by

$$\Delta G_i = [\text{KW}_{n-i}\text{D}_i^+] \Delta G_i^0 = -NRT \beta_i y^i \ln (\beta_0 \beta_i) \{ 1 + \sum \beta_i y^i \}^{-1}$$

The total free energy of transfer ΔG_t of N mol/liter of potassium(I) from the purely aqueous medium to the mixed solvent medium is the sum of the contributions from each potassium(I) species present in the mixed solvent so that

$$\begin{aligned}\Delta G_t &= \sum_{i=0}^n \Delta G_i \\ &= -NRT \{1 + \sum \beta_i y^i\}^{-1} \{ \ln \beta_0 + \sum_{i=1}^n \beta_i y^i \ln (\beta_0 \beta_i) \}\end{aligned}\quad (4)$$

If each side of eqn (4) is divided by N to give the standard free energy of transfer ΔG_t^0 (K^+) per mol and if each side of eqn (4) is divided by $(-RT)$ to give a unitless ratio, G_{ij}^0 , for the molar standard free energy of transfer, eqn (4) becomes

$$\begin{aligned}G_{ij}^0 &= \{1 + \sum \beta_i y^i\}^{-1} \{ \ln \beta_0 + \sum_{i=1}^n \beta_i y^i (\ln \beta_0 + \ln \beta_i) \} \\ &= \{1 + \sum \beta_i y^i\}^{-1} \{ \ln \beta_0 (1 + \sum \beta_i y^i) + \sum \beta_i y^i \ln \beta_i \} \\ &\quad \frac{\sum \beta_i y^i \ln \beta_i}{1 + \sum \beta_i y^i}\end{aligned}\quad (5)$$

This equation applies to one solvent mixture in which the ratio of the activities of dimethyl sulfoxide and water is y and for which the unitless free energy of transfer is G_{ij}^0 and it is readily rearranged to give eqn (6) for the calculation of $\ln \beta_0$

$$\ln \beta_0 = G_{ij}^0 - \frac{g(\beta, y)}{f(\beta, y)}\quad (6)$$

where

$$g(\beta, y) = \sum_{i=1}^n \beta_i y^i \ln \beta_i\quad (7)$$

and

$$f(\beta, y) = 1 + \sum_{i=1}^n \beta_i y^i\quad (8)$$

Because eqn (6) involves no substitution of water by Me_2SO in the solvation sphere the constant β_0 should remain relatively constant over the range of solvent compositions $0 < X_D \leq 1$. A value of β_0 can be calculated for each solvent mixture and the average value $\bar{\beta}_0$ can be minimized and a best fit obtained from the experimental values of the activities of the solvents in the mixture and the free energies of transfer.

In order to calculate a value of $\ln \beta_0$ from eqn (6) the β_i ($i = 1, \dots, n$) must be known; for the case of the K^+ ion they are not known. Because eqn (5) is a transcendental equation one cannot obtain $(n+1)$ analytic expressions for the $(n+1)$ equilibrium constants $\beta_0, \beta_1, \dots, \beta_n$ in terms of known experimental quantities only. Trial and error methods can be adopted in this situation to obtain the best fit to the experimental data. However minimizing the error in β_0 with respect to n β_i values when n was also unknown was not attempted. Instead a modified Covington¹⁴ approach was adopted to reduce the number of parameters.

In this modified approach $\beta_i = nx$ which defines x because n is the statistical factor for the first stepwise substitution of KW_n^+ . Succeeding β_i are given as a product of the appropriate statistical factor, x and a power of the parameter k referred to in the introduction; thus

$$\beta_i = \binom{n+1-i}{i} x^i k^i \quad (9)$$

In the Covington approach, k to the first power appeared in the second stepwise substitution constant and the power of k increased by unity with each succeeding stepwise substitution. Thus the free energy change of each stepwise substitution reaction after the first substitution changed regularly by $-RT \ln k$ (aside from the changes caused by changing statistical factors) as the substitution progressed. We found this feature of a regular change after the first substitution step to be very unsatisfactory in the case of K^+ . We allowed the power of k in β_i ($i = 2, \dots, n$) to be more flexible and in effect minimized the percentage standard deviation of $\bar{\beta}_0$ with respect to the powers of k in these β_i . Thus our model of the solvated K^+ ion included n, x, k and the powers of k in each β_i ($i = 2, \dots, n$) as parameters.

RESULTS AND DISCUSSION

The solvation number $n = 14$ gave the smallest percentage standard deviation, $\% \sigma$, for β_0 when the following expressions were used for the fourteen stepwise formation constants required for the substitution of fourteen water molecules by fourteen Me_2SO molecules:

$$K_1 = 14x, K_2 = 6.5x, K_3 = 4x, K_4 = 2.75x, K_5 = 2x,$$

$$K_6 = 1.5x, K_7 = ({}^6/7) kx, K_8 = ({}^7/8) kx, K_9 = ({}^2/3) kx,$$

$$K_{10} = 0.5 kx, K_{11} = ({}^{11}/1) k^2x, K_{12} = 0.25 k^2x, K_{13} = ({}^2/13) k^2x, K_{14} = ({}^1/14) k^4x.$$

The numerical factors are, of course, the statistical factors due to numbers of solvent molecules in the solvation sphere. These stepwise formation constants gave:

$$\beta_0 = 1.40 (\pm 31.4\%)$$

for water + Me_2SO solvent mixtures in the range $0.1 \leq X_D \leq 0.9$ for $k = 3.847$ and $x = 0.35021$.

The percentage standard deviation increased when the values of k and x were either increased or decreased by 1 or more in the last significant digit given. The error in $\bar{\beta}_0$ also increased if any of the powers of k (as given above) were increased or decreased. (It should be noted that the first six stepwise formation constants contain $k^0 = 1$.) For any solvation number n , once the power of k was increased in a K_i it could not be decreased in any succeeding K_i without increasing the error. For example in the K_i given above, once k was introduced in K_7 all succeeding K_i had to contain a power of k greater than or equal to unity or the error would increase. Likewise once k^2 was introduced in K_{11} all succeeding K_i had to contain a power of k greater than or equal to 2 or the error would increase. The position in the K_i ($i = 2, \dots, n$) sequence at which to increase the power of k was found by trial and error. Negative powers of k were not used to begin the sequence of equal and algebraically increasing powers of k in the K_i because a successful application of an initially negative power in reducing error simply meant that the inverse value of k should be used with a positive power.

The most remarkable result given by the minimization of error process was that *powers of k greater than zero should not be introduced into K_2 to K_6 inclusive* (recall that K_1 defines x) and that *the use of k^0 should not be extended beyond K_6* . This result was obtained for $n = 12$ and 13 as well although the percent standard deviation for $\bar{\beta}_0$ was larger for these two n values than for $n = 14$. For $n > 14$ (where the error in β_0 was larger than for $n = 14$) it was found that k^0 should appear in the first seven K_i but not beyond.

In total the results strongly suggest that the K^+ ion has a unique inner solvation shell with six solvent molecules in it for which the stepwise formation constants K_2 to K_6 inclusive are adequately given by K_1 and the statistical factors involved for the solvent exchange examined here. Except for the statistical factors the free energy change in the stepwise replacement of each of these six water molecules is adequately given by

$$\Delta G = -RT \ln x = 2600 \text{ J mol}^{-1} \quad (10)$$

When the statistical factors are combined with the x value the stepwise free energy change ranges from $-RT \ln K_1 = -3940 \text{ J mol}^{-1}$ for the first step to $-RT \ln K_6 = +1600 \text{ J mol}^{-1}$ for the sixth step. The absolute values of the energies are all of the order of $(3/2)RT$ or less so the results are not in disagreement with the known lability of K^+ . Of course it is realized that a small overall free energy change for any one step does not necessarily mean lability for that step; there could be large activation free energies for the forward and reverse processes in that substitution step but that is unlikely to be the case here. When the overall free energy changes of the first six steps are calculated from the β_i ($i = 1, \dots, 6$) they are all found to be negative. This could be interpreted as K^+ having a preference for Me_2SO , as compared to water, in the inner solvation shell.

In searching for minima in $\% \sigma$ of $\bar{\beta}_0$ the range of k was taken to be $0.0001 \leq k \leq 1000$. It was felt that $-RT \ln 10^3 = -17 \text{ kJ mol}^{-1}$ and $-RT \ln 10^{-4} = 23 \text{ kJ mol}^{-1}$ were algebraically smaller and larger, respectively, than the change in ΔG for a single substitution step was likely to be. Within this range of k , many values were selected that differed only by a factor of 2 from each other (*e.g.*, 1000, 500, 250, 125, ...) throughout the entire range. This was more than adequate because whenever a k value gave a minimum error the presence of the minimum was indicated over a range of more than ten-fold in the k value (*e.g.*, the minimum at $k = 3.847$ was easily discernible in the k range $1 \leq k \leq 10$ and even greater). For each k value selected a range of x values would be searched for evidence of a minimum. Depending on the number, power and distribution of the k factors more than one minimum might be found but only one would yield a smallest value of $\% \sigma$. It is felt that no significant minimum was missed. The value $k = 3.847$ (which together with $x = .35021$ gave a minimum for $\% \sigma$) yields eqn (11):

$$\Delta(\Delta G) = -RT \ln k^m = -3340 \text{ m J mol}^{-1} \quad (11)$$

for the change in the free energy of a substitution step having k^m in the K_i expression as compared to just x (excluding contributions from changing statistical factors in this discussion). The free energy change of a substitution

step became more negative whenever the power of k increased in K_i for that step. An increase (or increases) was (were) always required toward the end of the substitution process whatever the value of n . (For $n = 14$ the increased powers of k were required in K_{11} and K_{14} in order to obtain a better fit of data.) This need for an increase in the power of k seemed to be caused by the free energies of transfer of K^+ being »too negative« at $X_D \geq 0.8$. The »too negative« values of $\Delta G_i^0(K^+)$ may in turn result from the fact that at $X_D \geq 0.8$ the Me_2SO does not have sufficient water to bond to in the bulk solvent phase so that transfer of Me_2SO from the bulk phase to the solvation sphere becomes easier. This result is in accord with the known properties of DMSO — water solutions.

The value of $\bar{\beta}_0 = 1.40$ is of the order of unity as expected because the differences in the interactions of the KW_{14}^+ species with the bulk solvent should be small as one solvent with a large dielectric constant is replaced by another solvent with a large dielectric constant. The percentage standard deviation for a single determination of β_0 was 31.4% for the range of solvent mixtures $0.1 \leq X_D \leq 0.9$. This error is considered to be quite satisfactory in view of the wide range of values embraced by some of the coefficients of the β_i in eqn (6). For example, the value of y ranges from 0.01564 for $X_D = 0.1$ to 30.06 for $X_D = 0.9$ and y^{14} ranges from 5.2×10^{-26} to 4.9×10^{20} over the same concentration range. As a result the parameters being determined must fit the data well at all concentrations because all concentrations are important in contributing to the value of $\ln \beta_0$ in eqn (6).

The numerical values of the β_i ($i = 1, \dots, 14$) obtained were:

$$\begin{aligned} \beta_1 &= 4.90, \beta_2 = 11.2, \beta_3 = 15.6, \beta_4 = 15.1, \beta_5 = 10.5, \\ \beta_6 &= 5.54, \beta_7 = 8.53, \beta_8 = 10.1, \beta_9 = 9.03, \beta_{10} = 6.08, \\ \beta_{11} &= 11.5, \beta_{12} = 14.9, \beta_{13} = 11.8, \beta_{14} = 64.9. \end{aligned}$$

The numerical values of the free energies for forming the fifteen $\text{KW}_{14-i}\text{D}_i^+$ ($i = 0, 1, \dots, 14$) ions from $\text{KW}_{14}^+(\text{aq})$ were obtained from equilibrium constants of reactions (0), (1b), ..., (ib), ..., (nb) and are, respectively, in joule mol⁻¹: $\Delta G_{10}^0 = -842$; $\Delta G_{11}^0 = -4784$; $\Delta G_{12}^0 = -6823$; $\Delta G_{13}^0 = -7658$; $\Delta G_{14}^0 = -7575$; $\Delta G_{15}^0 = -6682$; $\Delta G_{16}^0 = -5086$; $\Delta G_{17}^0 = -6156$; $\Delta G_{18}^0 = -6564$; $\Delta G_{19}^0 = -6298$; $\Delta G_{110}^0 = -5319$; $\Delta G_{111}^0 = -6890$; $\Delta G_{112}^0 = -7532$; $\Delta G_{113}^0 = -6971$; $\Delta G_{114}^0 = -11,187$. These values are all reasonable. To very limited extent such ΔG_{1i}^0 values could be used to help reject trial distributions of k^m among the K_i . If positive values of some ΔG_{1i}^0 appeared among the otherwise all negative values this was considered to be chemically unrealistic and the trial distribution rejected. In every case where this occurred the distribution would have been rejected anyway on the basis of the magnitude of the error in $\bar{\beta}_0$.

The β_i and ΔG_{1i}^0 given above were used to calculate values of $\Delta G_{1i}^0(K^+)$ for various solvent mixtures for comparison with the experimental values given by eqn (A). The comparison is made in Table I. The fit is the best that could be obtained and it is reasonably satisfactory.

TABLE I

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

X_D^a	ΔG_t° (expt) ^b	ΔG_t° (calc) ^b
0.10	— 0.91	— 1.1
0.15	— 1.7	— 1.5
0.20	— 2.5	— 2.1
0.25	— 3.5	— 3.0
0.30	— 4.5	— 4.2
0.35	— 5.5	— 5.4
0.40	— 6.5	— 6.4
0.45	— 7.4	— 8.2
0.50	— 8.3 ^c	—10.1
0.55	— 9.0 ^c	—10.6
0.60	— 9.7 ^c	—10.8
0.65	—10.3	—10.9
0.70	—10.8	—11.0
0.75	—11.2	—11.1
0.80	—11.6	—11.1
0.85	—12.0	—11.1
0.90	—12.4	—11.2

^a Mol fraction of dimethyl sulfoxide based on solvents only. ^b KJ mol⁻¹. ^c This experimental value never fit well for the minimum error in β_0 for any solvation number.

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SAŽETAK

Solvatacija kalijeveg iona u vodi i smjesi vode i dimetilsulfoksida

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Za spomenuta otapala dobiven je model solvatacije kalijeveg iona, korištenjem izmjenjenog Covingtonovog pristupa. Ustanovljeno je da šest od ukupno 14 molekula otapala uključenih u solvataciju, čine unutarnju solvatacijsku ljusku, dok ih osam čini vanjsku solvatacijsku ljusku. Određene su konstante ravnoteže izmjene molekula vode s molekulama dimetilsulfoksida u solvatacijskim ljuskama.