

The Microscopic Free Energies of Solvation for K^+ , Rb^+ and Cs^+ in Mixed Methanol (MeOH)-Dimethylformamide (DMFA) Solvents at 298.15 K

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Abstract The microscopic charging (ΔG_t charging), ion-dipole (ΔG_t ion-dipole) and ion-induced dipole (ΔG_t ion-induced dipole) free energies of transfer for some ions from methanol to mixed methanol (MeOH)-dimethylformamide (DMFA) solvents were calculated. These ions are potassium, rubidium and cesium. These theoretical free energies were compared with that of experimental values and the difference excess free energies of solvation were discussed. It was observed that the excess free energies for all ions are positive and follow the following order:

$$\Delta G_T(\text{excess}) K^+ > \Delta G_T(\text{excess}) Rb^+ > \Delta G_T(\text{excess}) Cs^+.$$

Indicating more solvation behaviour by increasing the percentage of DMFA in the mixed solvents due to more attraction of these ions in the range rich in DMFA

Keywords Microscopic free energy, potassium, rubidium, cesium, excess free energy, organic solvents

1. Calculations and Results

The electrostatic free energies of transfer ΔG_t (el) is known as the microscopic free energies of interaction[1]. The solvation free energies of ions is important in the applications of all fields, chemistry, physics and theoretical sciences to obtain the corresponding energies of salts. Also chemical reactions can be theoretically expected to happen by knowing the free energy values for reactants and products. When we know the free energies of the ions we can easily obtain that for any simple, heavy element, lanthanide and actinide salts, which facilitate the explanation of different reactions. The solvation free energy of an ion has been formulated by number of authors cited by Covington[1] as a composite of neutral and electrostatic contribution. A neutral part may be considered to be equivalent to the solvation energy of uncharged molecules analogous to the ion in structure and size. The electrostatic contribution of the free energy is not exactly evaluated before. In this work we did simple view to evaluate the electrostatic free energies and compare it with the available experimental values done by using the asymmetric Ph_4AsPh_4B (tetraphenylarsonium tetraphenylborate) assumption for evaluating single ion thermodynamics [Popovych...][2].

Transfer values are the difference in the thermodynamic functions in solvents or mixed solvents and that of methanol as reference solvent. The electrostatic microscopic free energies of transfer is composite of energy contributions from charging a sphere, ion induced dipole, ion induced dipole/and the ion quadrupole interactions. The last one the ion-quadrupole interaction are very small that can be neglected[1]. The charging of sphere can be calculated by using Born equation[2]. Other microscopic terms may be evaluated according to Buckingham model[3]. The neutral free energy is almost the same for ions that having the same electronic shells. But the microscopic free energies are only different and need evaluation.

Table (1): Physical Parameters of MeOH and DMFA at 298.15 K.

Physical Properties	MeOH ^(a)	DMFA ^(a)
Diameter σ (in Å)	3.84	4.962
Dipole moment μ ($\times 10^{-18}$ esu)	1.76	3.82
Dielectric Constant ϵ	32.7	36.8 ^(b)
Polarizability α ($\times 10^{-24}$ cm ³)	3.26	7.88

(a) ref. :7

(b) ref. :8

2. Individual Microscopic Energies

The individual microscopic interaction energies are given below for positive ions K^+ , Rb^+ and Cs^+ .

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$$\Delta G_t(\text{el}), \text{charging} = -\frac{Nq^2}{2} \left(\frac{1}{r(s)} - \frac{1}{r(w)} - \left(\frac{1}{\varepsilon_s} - \frac{1}{\varepsilon_s} \right) \right) \quad (1)$$

$$\Delta G_t(\text{ion-dipole}) = 4 Nq \mu_s \left(\frac{1}{\sigma_s^2(+)} + \frac{1}{\sigma_s^2(-)} \right) + 4 Nq \mu_m \left(\frac{1}{\sigma_m^2(+)} + \frac{1}{\sigma_m^2(-)} \right) \quad (2)$$

$$\Delta G_t(\text{ion-induced dipole}) =$$

$$2Nq^2 \alpha_s \left(\frac{1}{\sigma_s^4(+)} + \frac{1}{\sigma_s^4(-)} \right) + 2Nq^2 \alpha_m \left(\frac{1}{\sigma_m^4(+)} + \frac{1}{\sigma_m^4(-)} \right) \quad (3)$$

N is the avogadro's number, q the effective charge density, μ and α are the dipole moment and polarizability, ε the dielectric constant, r the radius and σ is the interaction diameter. Small and m denote mixed solvent and methanol, respectively.

For the two oppositely charged ions of the same size, the energy contributions of ion-quadrupole interactions are equal but have opposite signs, so that on addition of them these energy terms cancel out[4]. Therefore the electrostatic free energy terms can be considered as the sum for all the microscopic free energies in pure solvents.

$$\Delta G(\text{el}) = \Delta G(\text{charging}) + \Delta G(\text{ion-dip}) + \Delta G(\text{ion-ind-dipole}) \dots (4)$$

3. Discussion

In binary solvents, it is expected that the solvent composition of the ions is different from the composition of the bulk solution. The greater the dipole moment of a molecule, the better the chance for this molecule to be at the vicinity of the ion. In binary solvents, the solvent composition described as the mole fraction of first solvent in the mixtures, X_{s1} in the vicinity of the ion, owing to the dipole effect is estimated by[5, 6].

Table (3). Microscopic free energies of solvation of potassium ion and its excess solvation free energies in mixed MeOH-DMFA solvents at 298.15 K (in K.J/mole).

X_s	ΔG_t	ΔG_t	ΔG_t	ΔG_T	$\Delta G_T(K^+)^{(a)}$	ΔG_T
DMFA	(charg)	(ion-dipole)	(ion-ind-dipole)	(K ⁺)(theor)	(Exp)	(excess)
1.0	+ 0.09673	-9.936	-0.4366	-10.275	-2.882	+7.340
0.8256	+0.00244	-9.9381	-0.4366	-10.372	-2.933	+7.439
0.6778	+0.00253	-9.9381	-0.4366	-10.372	-3.006	+7.366
0.5510	+0.00256	-9.4708	-0.3487	-9.8169	-2.930	+6.880
0.4410	+0.00247	-7.5590	-0.2792	-7.8350	-2.754	+5.081
0.3447	+0.00237	-5.9085	-0.2181	-6.1240	-2.607	+3.517
0.2596	+0.00216	-4.4500	-0.1643	-4.6120	-2.464	+2.140
0.1840	+0.00186	-3.1540	-0.1164	-3.2660	-2.197	+1.069
0.1164	+0.00148	-1.9948	-0.0737	-2.0670	-1.680	+0.382
0.0552	+0.00101	-0.9456	-0.035	-0.9796	-1.010	+0.030
0		0	0	0	0	0

(a) ref: 8

$$X_{s1} = X_s \left(\frac{\mu_s}{\sigma_s^2} \right) / \left(\frac{\mu_m}{\sigma_m^2} \right) \quad (5)$$

Where X_s is the mole fraction of methanol. A similar affect may be expected for ion-induced-dipole interaction such that the mole fraction thus influenced by:

$$X_{s2} = X_s \left(\frac{\alpha_s}{\sigma_s^4} \right) / \left(\frac{\alpha_m}{\sigma_m^4} \right)$$

For mixed solvents the electrostatic energies becomes:

$$\Delta G(\text{el}) X_s = \Delta G(\text{charging}) (X_s) + X_{s1}$$

$$\Delta G(\text{ion-dipole}) + X_{s2} \Delta G(\text{ion-induces}) \dots \dots \dots (7)$$

Equation 7.....equal equation. 8:

$$\Delta G_T = \Delta G_T(\text{charg.}) + \Delta G_T(\text{ion-dipole}) + \Delta G_T(\text{ion-ind-dipole}) \dots (8)$$

Table (2). Parameters X_{s1} and X_{s2} for mixed MeOH-DMFA solvents at 298.15 K.

X_s DMFA	X_{s1}	X_{s2}
1	1.00	1.00
0.8256	1.00	1.00
0.6778	1.00	1.00
0.5510	0.9597	0.8095
0.4410	0.7681	0.6479
0.3447	0.6004	0.5064
0.2596	0.4522	0.3814
0.1840	0.3205	0.2703
0.1164	0.2027	0.1711
0.0552	0.0961	0.0611
0	0	0

The physical parameters of DMFA and MeOH are shown in Table (1). The X_{s1} and X_{s2} calculated are cited in Table (2). All the solvated radii are taken from ref.8, the dielectric constants & dipole moments were calculated by summing the multiplication of each property by the mole fraction of each solvent in the binary mixture.

Table (4). Microscopic free energies of solvation for rubidium ion and its excess solvation free energies in mixed MeOH. DMFA solvents at 298.15 K (in KJ/mole).

X _s	ΔG_t	ΔG_t	ΔG_t	ΔG_T	$\Delta G_T(Rb^+)^a$	ΔG_T
DMFA	(charge)	(ion-dipole)	(ion-indu-dip-ind)	(Rb ⁺)(theor)	(Exp)	(excess)
1.0	+ 0.00204	-10.1322	-0.431	-10.5611	-3.112	+7.449
0.8256	+0.00206	-10.1322	-0.431	-10.5611	-3.162	+7.399
0.6778	+0.00214	-10.1322	-0.431	-10.561	3.138	+7.423
0.5510	+0.00221	-10.1322	-0.3476	-10.4775	-3.042	+7.435
0.4410	+0.00101	-8.5272	-0.2783	-8.8045	-2.856	+5.948
0.3447	+0.00201	-6.6657	-0.2175	-6.8824	-2.570	+4.312
0.2596	+0.00183	-5.0260	-0.1638	-5.1879	-2.142	+3.045
0.1840	+0.00158	-3.5581	-0.1160	-3.6725	-1.736	+2.936
0.1164	+0.00126	-2.2511	-0.0734	-2.3232	-1.226	+1.097
0.0552	+0.00086	-1.0668	-0.0347	-1.0064	-0.685	+0.415
0	0	0	0	0	0	0

(a) ref: 8

Table (5). Microscopic free energies of solvation for cesium ion and its excess solvation free energies in mixed MeOH-DMFA solvents at 298.15 K (in KJ/mole).

X _s	ΔG_t	ΔG_t	ΔG_t	ΔG_T	$\Delta G_T(Cs^+)^a$	ΔG_T
DMFA	(charge)	(ion-dipole)	(ion-ind-dip)	(Cs ⁺)(theor)	(Exp)	(excess)
1.0	+ 0.00204	-8.897	-0.4091	-9.304	-3.741	+5.563
0.8256	+0.00209	-8.897	-0.4091	-9.304	-3.638	+5.676
0.6778	+0.00216	-8.897	-0.4091	-9.3039	3.505	+5.799
0.5510	+0.00216	-8.897	-0.3825	-9.277	-3.298	+5.979
0.4410	+0.00212	-6.8298	-0.3062	-7.1338	-3.022	+4.1118
0.3440	+0.00201	-5.3383	-0.2393	-5.5756	-2.763	+2.812
0.2596	+0.00183	-4.0204	-0.1802	-4.1987	-2.435	+1.763
0.1840	+0.00157	-2.8499	-0.1277	-2.97600	-2.078	+0.898
0.1164	+0.00125	-1.803	-0.0807	-1.8824	-1.511	+0.37
0.0552	+0.00086	-0.8541	-0.0384	-0.8924	-0.779	+0.11
0	0	0	0	0	0	0

(a) ref: 8

4. Conclusions

All the calculated microscopic free energies for the ions under consideration were calculated and listed in Tables 3, 4 and 5. The total microscopic free energies calculated were compared with the experimental values taken from ref. 8 and the excess values were evaluated by applying equation[9-15].

$$\Delta G_T(\text{excess}) = \Delta G_T(\text{exp}) - \Delta G_T(\text{theor}).$$

It observed from Tables 3, 4 & 5 that the excess free energies for all ions are positive and follow the following order: $\Delta G_T(\text{excess}) K^+ > \Delta G_T(\text{excess}) Rb^+ > \Delta G_T(\text{excess}) Cs^+$. Indicating more solvation behaviour by increasing the percentage of DMFA in the mixed solvents due to more attraction of these ions in the range rich in DMFA. It was also concluded that the excess energies lie in the range between 90 to 94% as calculated from the references above ref. 2. This great part of the free energies is the neutral contribution which can be evaluated experimentally or calculated theoretically. Therefore on using such this work the electrostatic free energies can be calculated. On adding the neutral free energies to it we can obtain the whole free energies of solvation

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