

Solvation Free Energies of K^+ , Rb^+ and Cs^+ Ions in Methanol—*N,N*-dimethylformamide Mixtures

Esam A. Gomaa

Teachers Training College, Salalah — P. O. 19905, Sultanate of Oman

Received October 15, 1987

The selective solvation of K^+ , Rb^+ and Cs^+ ions has been studied at 25 °C by solubility measurements. The solubility of tetraphenylboride salts, $KBPh_4$, $RbBPh_4$ and $CsBPh_4$ increases with the addition of *N,N*-dimethylformamide (DMF) to methanol (CH_3OH) solutions. From the solubility data, the solvation free energies of the ions under consideration are evaluated on applying the asymmetric tetraphenylarsonium-tetraphenylboride ($\Delta G_t^\circ Ph_4As^+ > \Delta G_t^\circ Ph_4B^-$) assumption and their values are discussed.

INTRODUCTION

The solvation behaviour of single ions in mixed solvents can be easily discussed on knowing the free energy values of the interaction between these ions and the solvents. Extrathermodynamic assumptions¹⁻³ must be used for the estimation of single ion free energies. Among these assumptions, the Ph_4AsBPh_4 assumption attained increased acceptance.⁴⁻⁹ In 1978 it was proved by Kim that Ph_4AsBPh_4 is an asymmetric assumption (the free energies of transfer for the reference anion are slightly greater than that of the reference cation).¹⁰⁻¹² The present work deals with the determination of standard free energies of transfer of ions K^+ , Rb^+ and Cs^+ from methanol to mixed DMF- CH_3OH solvents using the new modified Ph_4AsBPh_4 assumption.

EXPERIMENTAL

The preparation of saturated solutions and the solubility measurements for $KBPh_4$, $RbBPh_4$ and $CsBPh_4$ have been described in a previous work.¹³ The saturated solutions were prepared in test tubes putting in a shaking water thermostat of the Assistant type. The salts were shaken in the water bath for one week and then left for two days without shaking to reach the necessary equilibrium. The solubilities were determined either gravimetrically or by spectrophotometry. CH_3OH and DMF extra pure from BDH Co. (spectroscopic grade) were used without purification other than introducing a drying agent for storage (molecular sieve).

RESULTS AND DISCUSSION

The electrostatic free energies of transfer ($\Delta G_t(\text{el})$) of Ph_4AsBPh_4 electrolyte and its individual ions from DMF to CH_3OH are known as a composite of energy contributions from charging a sphere, ion dipole, ion induced dipole and ion-quadrupole interactions. The charging of sphere energy can be calculated by using the Born equation.¹² Other energy terms may be

evaluated according to the Buckingham model.¹⁴ The individual interaction energies are given below for the positive reference cation (Ph_4As^+). In the case of the negative reference anion (Ph_4B^-), the sign of the interaction distance must be changed to $(-)$.

$$\Delta G_t(\text{el}), \text{ charging} = \frac{Nq^2}{a} \left(\frac{1}{r_1} - \frac{1}{r_2} \right) \left(\frac{1}{\epsilon_1} - \frac{1}{\epsilon_2} \right) \quad (1)$$

$$\Delta G_t(\text{el}), \text{ ion-dipole} = -4Nq\mu_1 \left(\frac{1}{\sigma_1^2(+)} + \frac{1}{\sigma_2^2(+)} \right) + 4Nq\mu_2 \cdot \left(\frac{1}{\sigma_1^2(+)} + \frac{1}{\sigma_2^2(+)} \right) \quad (2)$$

$$\Delta G_t(\text{el}), \text{ ion-induced-dipole} = -2Nq^2\alpha_1 \left(\frac{1}{\sigma_1^4(+)} + \frac{1}{\sigma_2^4(+)} \right) + 2Nq^2\alpha_2 \left(\frac{1}{\sigma_1^4(+)} + \frac{1}{\sigma_2^4(+)} \right) \quad (3)$$

where

N is the Avogadro's number, q the effective charge density of the reference ion, μ and α are the dipole moment and the polarizability, ϵ the dielectric constant, r the radius of the reference ion and σ is the interaction distance between the reference ion and the solvent molecules.¹² Subscripts 1 and 2 denote DMF and CH_3OH , respectively. The physical parameters of DMF, CH_3OH and the reference ions (Ph_4As^+ and Ph_4B^-) are shown in Table I. The calculated values for the individual free energies after eqs. (1–3) are listed in Table II. For the lack of the quadrupole moment of CH_3OH , at present it is not possible to estimate the very small energy contribution from the ion-quadrupole interaction.

TABLE I

Physical parameters of CH_3OH , DMF and the reference ions (Ph_4As^+ and Ph_4B^-)

Physical properties	Ph_4As^+	Ph_4B^-	CH_3OH	DMF
Hard sphere diameter: σ (Å)	4.28 ^a	4.21 ^a	3.84 ^b	4.96 ^b
Effective charge: q ($\times 10^{-10}$ esu)	1.004 ^a	1.004 ^a	—	—
Dipole moment: μ ($\times 10^{-18}$ esu)	0	0	1.76 ^b	3.82 ^b
Dielectric constant: ϵ	—	—	32.7 ^b	36.8 ^b
Polarizability: ($\times 10^{-24}$ cm ³)	—	—	3.26 ^c	7.88 ^c

^a Ref., 11, ^b ref., 15, ^c ref., 21.

TABLE II

Electrostatic contribution of standard free energies of transfer for the reference ions (Ph_4As^+ and Ph_4B^-) from DMF to CH_3OH at 25°C in kcal/mol

ΔG_t (el)	Ph_4As^+	Ph_4B^-	$\text{Ph}_4\text{AsBPh}_4$
ΔG_t (el) ion-dip.	-3.32	-3.38	-6.7
ΔG_t (el) ion-ind.	-0.1	-0.1	-0.2
ΔG_t (el) ion-quad.	—	—	~ 0
ΔG_t (el) charging	-0.01	-0.01	-0.02
ΔG_t (el) total-theoretical	-3.43	-3.49	-6.92
ΔG_t (el) total-experimental	-3.52	-3.29	-6.81

It can be concluded from Table II that there is a good agreement between the calculated values of ΔG_t (el) and the experimental values taken from ref. 15. This also proved that the $\text{Ph}_4\text{AsBPh}_4$ assumption is an asymmetric assumption.

For the calculation of the activity coefficients (γ_{\pm}) for the solutes KBPh_4 , RbBPh_4 and CsBPh_4 in mixed CH_3OH -DMF mixtures, the modified Debye — Hückel equation was used.¹¹⁻¹³

$$\log \gamma_{\pm} = - \frac{A Z_A Z_B \sqrt{S}}{1 + B a \sqrt{S}} \quad (4)$$

where $A = 1.825 \times 10^6 / (T \cdot \epsilon)^{3/2}$, $B = 50.29 \times 10^8 / (T \cdot \epsilon)^{1/2} \cdot T$ is the absolute temperature, S is the molal solubility and a is the solvated radius. a is the distance of the closest approach, estimated by assuming one solvent molecule being placed between ions. In binary solvents, the average sizes of the solvent molecules (σ°) were estimated by using an empirical relation published by Kim.¹¹ Thus, the calculated diameters (σ°) from the density measurements in the previous work¹⁵ are listed in Table III. With the help of σ° , the distance of the closest approach was calculated by the relation $a = r_+ + \sigma^\circ + r_-$, where r_+ and r_- represent the crystal radii of the cations and the van der Waals radius of reference anion, respectively.¹⁰ Their values are also seen in Table III. The solubility products of KBPh_4 , RbBPh_4 and CsBPh_4 are

TABLE III

Solvent diameters (σ°) and the solvated radii of KBPh_4 , RbBPh_4 and CsBPh_4 in mixed CH_3OH -DMF solvents at 25°C in \AA

Mole fraction (X_i) of CH_3OH	σ°	a KBPh_4	a RbBPh_4	a CsBPh_4
0	4.962	10.54	10.69	10.90
0.174	4.791	10.40	10.55	10.77
0.322	4.627	10.24	10.38	10.59
0.449	4.482	10.09	10.24	10.45
0.559	4.353	9.96	10.11	10.32
0.655	4.240	9.85	10.00	10.21
0.740	4.128	9.74	9.88	10.09
0.816	4.044	9.65	9.80	10.01
0.884	3.957	9.57	9.72	9.93
0.945	3.912	9.52	9.67	9.88
1.0	3.796	9.31	9.46	9.67

determined in the molal scale and their activity coefficient values are tabulated in Table IV. The literature solubility value was 3.11×10^{-3} (mole/l)

TABLE IV

Molal solubilities (S), activity coefficients ($\log \gamma_{\pm}$) and pK_{sp} 's for $KBPh_4$, $RbBPh_4$ and $CsBPh_4$ in mixed CH_3OH -DMF solvents at $25^\circ C$

X_s CH_3OH	KBPh ₄			RbBPh ₄			CsBPh ₄		
	S	$\log \gamma_{\pm}$	pK_{sp}	S	$\log \gamma_{\pm}$	pK_{sp}	S	$\log \gamma_{\pm}$	pK_{sp}
0	1.336	-0.269	0.286	0.749	-0.294	0.838	0.484	-0.239	1.112
0.174	1.151	-0.267	0.417	0.583	-0.251	0.970	0.360	-0.234	1.356
0.322	0.921	-0.267	0.605	0.446	-0.245	1.193	0.248	-0.224	1.659
0.449	0.712	-0.264	0.823	0.322	-0.238	1.461	0.161	-0.212	2.009
0.559	0.495	-0.258	1.127	0.216	-0.224	1.778	0.101	-0.198	2.387
0.655	0.322	-0.249	1.455	0.129	-0.213	2.201	0.060	-0.180	2.797
0.740	0.212	-0.238	1.824	0.063	-0.187	2.781	0.032	-0.157	3.301
0.816	0.122	-0.221	2.269	0.031	-0.166	3.328	0.017	-0.133	3.811
0.884	5.31×10^{-2}	-0.190	2.930	1.46×10^{-2}	-0.132	3.988	7.0×10^{-3}	-0.102	4.514
0.944	1.88×10^{-2}	-0.148	3.75	5.54×10^{-3}	-0.097	4.707	2.42×10^{-3}	-0.071	5.373
1.0	4.94×10^{-3}	-0.099	4.811	2.01×10^{-3}	-0.069	5.531	8.21×10^{-4}	-0.047	6.267

in the molar scale,¹⁶ which differs from the here estimated value in the molal scale and also the previously estimated ones.¹⁷ The transfer free energies from methanol to mixed CH_3OH -DMF for $KBPh_4$, $RbBPh_4$ and $CsBPh_4$ are calculated by the use of equation 5.

$$\Delta G_t^\circ = -2.303 RT [pK_{sp(1)} - pK_{sp(2)}] \quad (5)$$

where $pK_{sp} (= -2 \log S + 2 \log \gamma_{\pm})$ are the solubility products of the salts in DMF and mixed solvents (1) and in pure CH_3OH (2). The values calculated by eq. 5 are demonstrated in Table V. Subtracting ΔG_t° of tetraphenylboride salts from that of the reference anion, Ph_4B^- , given in ref. 15, the individual free energies of transfer of the ions K^+ , Rb^+ and Cs^+ are obtained. Their values are shown in Table V.

TABLE V

Solvation free energies (ΔG_t°) of transfer for $KBPh_4$, $RbBPh_4$ and $CsBPh_4$ from DMF to mixed CH_3OH -DMF solvents and their single ion free energies at $25^\circ C$ (kcal/mol)

X_s CH_3OH	KBPh ₄	K ⁺	RbBPh ₄	Rb ⁺	CsBPh ₄	Cs ⁺
0	-6.172	-2.882	-9.129	-3.112	-7.031	-3.741
0.174	-5.993	-2.933	-8.949	-3.162	-6.698	-3.638
0.322	-5.786	-3.006	-8.646	-3.138	-6.285	-3.505
0.449	-5.440	-2.930	-8.279	-3.042	-5.808	-3.298
0.559	-5.024	-2.754	-7.847	-2.856	-5.292	-3.022
0.655	-4.577	-2.607	-7.270	-2.570	-4.733	-2.763
0.740	-4.074	-2.464	-6.479	-2.142	-4.045	-2.435
0.816	-3.460	-2.197	-5.733	-1.736	-3.349	-2.078
0.884	-2.560	-1.680	-4.833	-1.226	-2.391	-1.511
0.945	-1.450	-1.010	-3.852	-0.685	-1.219	-0.779
1.0	0	0	0	0	0	0

Recently, the $\text{Ph}_4\text{AsBPh}_4$ assumption was strongly supported by Kim¹⁸ for the estimation of single ion free energies. It was also mentioned by Kim¹⁸ that the $\text{Ph}_4\text{SbBPh}_4$ assumption was also applicable as a thermodynamic assumption for the evaluation of single ion thermodynamics. On using both $\text{Ph}_4\text{AsBPh}_4$ and $\text{Ph}_4\text{SbBPh}_4$ assumptions the single ion free energies for K^+ , Rb^+ and Cs^+ ions in mixed CH_3OH -DMF will be the same because both assumptions belong the same reference anion (Ph_4B^-).

The literature single ion free energies for K^+ , Rb^+ and Cs^+ for transfer from CH_3OH to DMF are shown in Table VI on using the assumptions $\Delta G_i^\circ(\text{Me}_4\text{N}^+) = 0$ ¹⁹ and the symmetric $\text{Ph}_4\text{AsBPh}_4$ ^{4,20} giving data which slightly differ from each other for the cations under consideration.

TABLE VI

Literature solvation free energies for K^+ , Rb^+ and Cs^+ ions from dimethylformamide (DMF) to methanol (CH_3OH) in kcal/mole

Ion	(a)	(b)	(c)	(d)
K^+	-1.15	-4.70	-4.760	-2.882
Rb^+	-1.25	-4.80	-4.613	-3.112
Cs^+	-1.25	-4.50	-4.708	-3.741

(a) Based on $\Delta G_i^\circ(\text{Me}_4\text{N}^+) = 0$ ¹⁹ (b) Based on $\Delta G_i^\circ(\text{Ph}_4\text{As}^+) = \Delta G_i^\circ(\text{Ph}_4\text{B}^-)$ ⁴ (c) Based on $\Delta G_i^\circ(\text{Ph}_4\text{As}^+) = \Delta G_i^\circ(\text{Ph}_4\text{B}^-)$ at 30 °C.²⁰ (d) This work based on $\Delta G_i^\circ(\text{Ph}_4\text{As}^+) > \Delta G_i^\circ(\text{Ph}_4\text{B}^-)$.

The three ions (K^+ , Rb^+ and Cs^+) have the same tendency in solvation free energies in mixed CH_3OH -DMF solvents but differ in their values. Cs^+ values are greater than that of Rb^+ and K^+ data. Therefore, it is concluded that these ions are more selective solvated by methanol than DMF in their mixed solvents due to the stabilization in CH_3OH .

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SAŽETAK**Slobodne entalpije solvatacije iona K^+ , Rb^+ i Cs^+ u otopinama s miješanim otapalom etanol + N,N -dimetilformamid***E. A. Gomaa*

Metodom topljivosti određene su slobodne entalpije solvatacije iona K^+ , Rb^+ i Cs^+ pri 25 °C. Topljivost kalij-tetrafenilborida, rubidij-tetrafenilborida i cezij-tetrafenilborida raste s dodatkom N,N -dimetilformamida metanolnim otopinama soli. Slobodne entalpije solvatacije izračunavane su iz eksperimentalnih podataka o topljivosti uz primjenu asimetrične premise $\Delta G_i^\circ Ph_4As^+ > \Delta G_i^\circ Ph_4B^-$.