J. King Saud Univ., Vol. 3, *Science* (1), pp. 69-76 (1411/1991)

Application of the Scaled Particle Theory for the Solvation of Silver Tetraphenyl-Boride in Dimethylformamide-Water Mixtures at 298.15 K

Esam A. Gomaa

*Department of Chemistry, Faculty of Science, Mansoura University, Mansoura, Egypt**

(Received 17 October 1988; accepted for publication 16 January 1990)

Abstract. From solubility measurements of silver tetraphenyl-boride (STPB) at 298.15 K in DMF-H_2O mixtures, the free energies of transfer ($\Delta_w^s G^\circ$) from water to the mixed solvents were estimated. Theoretical calculation of the micro solute-solvent interactions for STPB in DMF-H_2O solvents were computed using the scaled particle theory (SPT). Experimental and theoretical free energies for STPB are compared and solute-solvent interactions discussed.

Introduction

Pierotti [1] applied the scaled particle theory [2] to estimate solubilities, heats, entropies and molar capacities of solutions. Reasonably good agreement between theory and experiment for evaluating the thermodynamic has been obtained for a number of neutral compounds and gases in a variety of solvents [3-7]. The aim of the present work is to extend the applicability of the scaled particle theory for the electrolyte silver tetraphenylboride (STPB) in mixed DMF-H_2O solvents.

Experimental

STPB was prepared by adding $NaPh_4B$ (Merck) to $AgNO_3$ (Merck) in aqueous solutions until complete precipitation of the salt. The precipitate was filtered and recrystallised in water. Exposure to light was prevented by keeping in a dark bottle. The distilled water used resulted from Millipore water purification system by passing

---

**Present address: Teachers Training College, Salalah, P.O. Box 19905. Sultanate of Oman* the first distilled water through four columns containing ion exchange resins and organic absorbent substances in the ready made EPA Est. 41237-MA-1 apparatus. The distilled water has a conductivity of $10^{-18}\Omega^{-1}$. Saturated solutions were prepared by shaking pure DMF (merck) and mixed solvents (300ml) with an excess of STPB till solid residue remained. Shaking water bath "Assistant" was used at a temperature of 25.0 ± 0.1°C and put in dark place. The shaking process took place for three days, followed by another one day without shaking to reach the necessary equilibrium. The concentration of STPB was determined gravimetrically except in water. The gravimetric method consisted of gradual evaporation of the saturated solutions (100 ml) in small beakers by I.R. lamp till dryness and weighing the precipitates. The solubility of STPB in water was determined by shaking saturated solution (1 1) with chloroform (10ml) in a separating funnel. The chloroform layer was extracted, sealed, irradiated for 1 hr (1 h) in a reactor (Forschung Reaktor, T.U. München, West Germany) and the activated ^{110}Ag ($T_{1/2}$ = 250 d) was measured by γ-spectrophotometer with a Ge(Li) detector coupled to a ND-420 multichannel γ-analyser as explained previously [8].

Results and Discussion

The solubilities (S) of STPB (molal scale) in DMF-H_2O at 298.15 K given in Table 1 are the mean values of three separate determinations. The thermodynamic solubility products of STPB (pK^o_{sp}) were calculated according to Equation 1.

$$pK^o_{sp} = -\log S^2 + 2\log \gamma_\pm \tag{1}$$

The activity coefficients ($\gamma_\pm$) estimated from the extended form of the Debye-Hückel equation [8], are also included in Table 1. Other physical parameters [9], namely the hard sphere diameters (σ), densities (d) and dielectric constants (ε) are given in Table 1. The solubility products of STPB show an average deviation of ± 0.3.

The free energies of transfer (ΔG^o_t) of STPB from water (w) as reference solvent to DMF and mixed solvents (s), were computed according to

$$\Delta\, {}^{s}_{w}G^o = \Delta G^o_t = 2.303\, RT\ [pK^o_{sp(s)} - pK^o_{sp(w)}] \tag{2}$$

The ΔG^o_t values could be divided into electrostatic ΔG^o_t (el) and non-electrostatic free energies $\Delta G^o_t(N)$ parts [10]. The electrostatic free energies were calculated by the Born equation [9] as:

$$\Delta G^o_t\,(el) = \frac{694.1}{r}\left(\frac{1}{\varepsilon} - 0.012\right) \tag{3}$$

where r is the STPB solvated radii. This is the sum of the crystal radius of silver ion, Van der Waals tetraphenylboride ion radius and the scaled particle theory diameters of the mixed solvents [11]. Subtracting ΔG_t^o (el) from ΔG_t^o values the neutral free energies ΔG_t^o (N) of STPB were obtained. The calculated ΔG_t^o, ΔG_t^o (el) and ΔG_t^o (N) values for STPB in mixed DMF-H_2O solvents are given in Table 1. It can be seen that ΔG_t^o and ΔG_t^o (N) increase (become more negative) while ΔG_t^o (el) becomes more positive as mole fraction of DMF increase.

Table 1. Log solubilities and the experimental free energies (kJ mol^{-1}) of STPB in mixed DMF-H_2O solvents at 298.15 K.

X_s DMF	Diameter σ in A°	Density (d) g/cm^3	ε	$-\log S^{(a)}$	$\gamma_\pm$
0	2.77	0.9971	78.5	8.790	0.99
0.259	3.329	0.9932	58.3	5.950	0.99
0.352	3.532	0.9875	53.7	5.250	0.99
0.483	3.813	0.9776	48.7	4.350	0.99
0.677	4.233	0.9628	43.0	3.475	0.98
1.0	4.930	0.9439	37.3	3.300	0.97

X_s DMF	pK_{sp}^o	ΔG_t^o	ΔG_t^o(el)	ΔG_t^o(N)
0	17.580$^{(b)}$	0	0	0
0.259	11.902	− 32.405	1.423	− 33.828
0.352	10.502	− 40.392	1.879	− 42.271
0.483	8.707	− 50.639	2.414	− 53.053
0.677	6.976	− 60.517	3.134	− 63.651
1.0	6.6222$^{(c)}$	− 62.534	3.887	− 66.421

(a) Solubility (S) in mol kg^{-1}.

(b) Same value given by, Kim, J.I.,Z. Phys. Chem., N.F., *121*, 1 (1980).

(c) The value of S is given by Badoz-Lambling, J. and Bardin, J.C., Electrochimica Acta, *19*, 725 (1974).

According to the scaled particle theory [1], solvation occurs through the primary formation of a cavity of the solute in the solvent(C) followed by their interaction (i). Following Pierotti [1], the cavity energy (G_C) is given by:

$$G_C = -RT\left\{\ln(1-Y) - \left(\frac{3Y}{1-Y}\right)R_{1,2} - \left[\left(\frac{3Y}{1-Y}\right) + 9/2\left(\frac{Y}{1-Y}\right)^2\right]R_{1,2}^2\right\} + \frac{NYP}{\rho}.\,R_{1,2}^3 \qquad (4)$$

where the packing density $Y = \pi \rho \sigma_1^3/6$, $\rho = N/V_1^0$, N Avogadro's number, V_1^o the molar volume, pressure P = 1 atm. and $R_{1,2} = \sigma_2 / \sigma_1$. From G_C values obtained for STPB in the mixed solvents from that of water. The estimated packing density (Y), G_C and ΔG_C values for STPB are included in Table 2. On the other hand, the interaction free energy (G_i) is a composite function incorporating dispersion-(G_L), induced-(G_{ind}), volume (G_v) and dipole-dipole free energies ($G_{dip\text{-}dip}$). These terms are computed as follows:

Table 2. Coefficients Y and the theoretical free energies of solvation (kJ mol^{-1}) of STPB in mixed DMF-H_2O solvents at 298.15 K.

X_s DMF	Y	G_C	ΔG_C	G_L	ΔG_L
0	1.564×10^{22}	114.156	0	2.455	0
0.259	27.040×10^{21}	107.679	− 11.474	2.793	0.338
0.352	32.123×10^{21}	98.529	− 15.627	2.943	0.488
0.483	40.026×10^{21}	92.755	− 21.401	3.177	0.722
0.677	53.917×10^{21}	84.149	− 30.009	3.561	1.106
1.0	88.209×10^{21}	69.856	− 44.208	4.298	1.843

X_s DMF	ΔG_{ind}	G_{ind}	G_v	ΔG_v	ΔG_{sum}
0	5.929	0	− 8.482	0	0
0.259	6.085	0.156	− 9.926	−1.444	− 12.422
0.352	6.299	0.370	−10.291	− 1.802	−16.569
0.483	6.654	0.725	−10.742	−2.259	−22.213
0.677	7.237	1.718	−11.337	−2.855	−30.037
1.0	4.591	−1.338	−12.059	−3.577	−47.279

(a) The dispersion free energy (G_L) is given by the relation:

$$G_L = -\,32/9\, R\pi \rho\, \sigma_{1,2}^3 \sqrt{\frac{\varepsilon_1}{k} \cdot \frac{\varepsilon_2}{k}} \qquad (5)$$

where $\sigma_{1,2} = 1/2\,(\sigma_1 + \sigma_2)$, ε_1/k, ε_2/k are energy parameters for the mixed solvents and STPB, respectively. The energy parameter ε_1/k was obtained by adding (summation) the multiplied values of the mole fraction with the energy parameters for both DMF and H_2O taken from the literature [12]. The ε_2/k for STPB was calculated from a semiemperical reaction between the bond strength and the energy parameters (ε/k) for some ions and found to be 20K.

b) The induced free energies (G_{ind}) were calculated according to:

$$G_{ind} = -\,12/9\,N\,\pi\,\rho\,\mu_1^2 \;\frac{\alpha^2}{\sigma_{1,2}^3} \tag{6}$$

where μ_1 is the dipole moment of the mixed solvents [5] and α_2 is the polarizability of the solute.

c) The free energy of volume formation was calculated following the relationship [3]:

$$G_v = RT\ln\frac{RT}{V} \tag{7}$$

where $V = x_1M_1 + x_2M_2/d$, x_1 and x_2 are the mole fraction of solvent and solute and M_1, M_2 their molecular weights. d is the density of the mixed solvent used. The three specified energies and their transfer values are grouped in Table 2. The sum of ΔG_C, ΔG_L, ΔG_{ind} and ΔG_v give ΔG_{sum} values for STPB in mixed DMF-H_2O mixtures (see Table 2). The free energies of the silver ion in mixed DMF-H_2O solvents were obtained by subtracting the ΔG_t° values of BPh_4^- ion, given in ref. [9] from that of STPB. These data, together with $\Delta G_{t(dip\text{-}dip)}$ for STPB are shown in Table 3.

Since the solubilities of STPB in the mixed solvents under consideration are low, therefore, ion pair formation can be neglected.

Inspection of the figures of Table 2 reveals a difference between the ΔG_t° and the ΔG_{sum} values. This difference is apparently the result of the dipole-dipole interaction energy for both solute and solvent. The values of this term were calculated as in ref. [12] are given in Table 3.

Table 3. Free energies of transfer for Ph_4B^-, Ag^+ ions and the dipole-dipole free energies for the solvation of STPB from water to mixed DMF-H_2O solvents at 298.15 K. in kJ mol^{-1}

X_s DMF	ΔG_t° Ph_4B^-	ΔG_t° Ag^+	$\Delta G_{t(dip\text{-}dip)}$ STPB
0	0	0	0
0.259	− 22.175	− 11.652	− 21.447
0.352	− 26.066	− 16.205	− 25.702
0.483	− 30.752	− 22.300	− 30.840
0.677	− 34.727	− 28.923	− 33.610
1.0	− 38.911	− 28.221	− 19.142

This table shows that the free energy values for the silver ion increased (becomes more negative) with an increase of the DMF content in the solvent mixture. For comparison purposes the ΔG_t^o ($H_2O \rightarrow$ DMF) for some ions are included [13]. These values are -1.594, -33.079, 44.062, 29.242 & 21.025 kJ/mole for the ions K^+, Cs^+, Cl^-, Br^- and I^-, respectively. These literature values (based on the asymmetric Ph_4AsBPh_4 electrolyte thermodynamic assumption) indicate that DMF solvate the cations (negative values) preferentially than the anions (positive values) because this solvent contains basic oxygen. The abnormality of transfer free energy values for big anions and cations like Ph_4B^- (value) and Ph_4As^+ (value) is due to the increase in the dispersion forces of these ions [13]. The dipole-dipole free energies of STPB first increases and then decreases on the addition of DMF. The last behaviour may be attributed to the corresponding complexes which STPB builds up with the solvent molecules [14].

It is concluded that STPB is more stabilized in the mixed DMF-H_2O solvent system than in pure ,water.

References

[1] Pierotti, R.A. "Aqueous Solutions of Nonpolar Gases." *J. Phys. Chem.*, 69 (1965), 281-288.

[2] Reiss, H., Frisch, H.L. and Lebowitz, J.L. "Scaled Particle Theory." *J. Chem. Phys.*, 31 (1959), 361-388.

[3] Lucas, M. and Feilloly, A. "Prevision de l'enthalpie de dissolution de molécules non polaries dans les melanges eau-ethanol." *Bull-Soc. Chim. France*, 4 (1970), 1267-1270.

[4] Kim, J.I. and Brückl, N. "On the Temperature Dependence of Solubilities of Inert Gases from the Scaled Particle Theory." *Z. Phys. Chem., Neue Folge*, 110 (1978), 197-208.

[5] Brückl, N. and Kim, J.I. "Gibbs Free Energies of Solute-Solvent Interaction for He, Ne, Kr, Xe, H_2, O_2, N_2, CH_4, SF_6, C_2H_4, CO_2 and C_2H_2 in Various Solvents: Comparison of Theoretical Predication with Experiment." *Z. Phys. Chem., Neue Folge*, 126 (1981), 133-150.

[6] Gunnerson, F.S. and Cronenberg, A.W. "A Prediction of the Inert Gas Solubilities in Stoichometric Molten UO_2." *J. Nucl. Materials*, 58 (1971), 311-320.

[7] Treiner, C. "Use of the Scaled Particle Theory for the Determination of Single Ion Standard Free Energy of Transfer between Solvents." *Cand. J. Chem.*, 55 (1977), 682-685.

[8] Gomaa, E.A. "Solubility of Tetraphenyl Derivatives, Ph_4C, Ph_4Ge and Ph_4AsBPh_4 in Aqueous Hexamethylphosphortriamide Solutions at 25°C." *Ind. J. of Tech.* 24 (1986), 725-726.

[9] Kim, J.I., Cecal, A., Born, H.-J and Gomaa, E.A. "Preferential Solvation of Single Ions: A Critical Study of the Ph_4AsBPh_4 Assumption for Single Ion Thermodynamics in Mixed Aqueous-Acetonitrile and Aqueous-N, N-Dmethylformamide Solvents." *Z. Phys. Chem., Neue Folge*, 110 (1978), 209-227.

[10] Cox, B.G. "Thermodynamics of Ion-Solvent Interactions." *Chem. Soc. Rev.*, 9 (1980), 381-411.

[11] Kim, J.I. "The Ph_4AsBPh_4 Assumption for Single Ion Thermodynamics and its Asymmetric Partition to Cation and Anion." *Bull. Soc. Chim. Belg.*, 95 (1986), 435-446.

[12] Gomaa, E.A. "Theoretical Contribution of Solvation of AgBr in Some Organic Solvents at 25°C." *Thermochimica Acta*, 128 (1988), 99-103.

[13] Gomaa, E.A. "Solute-Solvent Interactions of some Univalent-Univalent Salts with Various Organic Solvents at 25°C." *Thermochimica Acta,* 120 (1987), 183-190.

[14] Kim, J.I. and Duschner, H. "Preferential Solvation of Single Ions: The Medium Effects of Ag^+, $AgCl_n^{1-n}$ and Cl^- Ions in Mixed-Acetonitrile-Water Systems." *Z. Phys. Chem., Neue Folge,* 106 (1977), 1-16.

تطبيق نظرية الجـزيء المختار لدراسة ذوبان بورن رباعي فينيل الفضة في مخاليط من الماء مع ثنائي ميثيل الفورماميد عند درجة حرارة ٢٩٨,١٥ درجة مطلقة

عصام عرفة حسن جمعة

*قسم الكيمياء، كلية العلوم، جامعة المنصورة، جمهورية مصر العربية**

(استلم في ٧ ربيع الأول ١٤٠٩هـ، قُبل للنشر في ١٩ جمادي الآخرة ١٤١٠هـ)

ملخص البحث. تم تعيين الطاقة الحرة لإنتقال بورن رباعي فينيل الفضة من الماء إلى مخاليط من الماء وثنـائي ميثيل الفورماميد من القياسات العملية للذوبانية عند رجة حرارة ٢٩٨,١٥ درجة مطلقة. تم كذلك تطبيق نظرية الجزيء المختار على ذوبان مركب الفضة السابق ذكره وقورنت النتائج بالمستنتجة معمليًا.

العنوان الحالي: ـ الكلية المتوسطة للمعلمين بصلالة ـ ص. ب ١٩٩٠٥ ـ سلطنة عمان.