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THEORETICAL CONTRIBUTION OF SOLVATION OF AgBr IN SOME ORGANIC SOLVENTS AT 25°C

ESAM A. GOMAA

Teachers Training College, Salālah-P.O. 19905 (Sultanate of Oman)

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ABSTRACT

The free energies of transfer of silver bromide from water to acetonitrile (MeCN), *N*-methylformamide (*N*-MF), ethanol (EtOH), *N*-*N*-dimethylformamide (DMF), propylene carbonate (PC), dimethylsulphoxide (DMSO) and *N*-methylpyrrolidone (*N*-MePy) were estimated from the experimental solubility measurements. The theoretical calculation of the free energies of transfer was also carried out using the hard sphere diameter method. Further calculations of the different parts of both the experimental and theoretical free energies of transfer of AgBr from water to the organic solvents were worked out and their values were compared.

INTRODUCTION

The solvation process of a solute in liquid solvents has been described theoretically by Pierotti [1–3] applying the hard sphere diameter method (scaled particle theory) [4–6]. This theory has been reasonably successful for calculating the solubilities of non-electrolytes in solvents [7].

This theory was originally developed as a formal statistical thermodynamic theory of dense fluids and provides relations relevant to the behaviour of real fluids.

This paper concentrates on the application of the Pierotti theory to calculate the free energies of solution of AgBr in some organic solvents and compares these values with those obtained experimentally.

EXPERIMENTAL

AgBr of the type Riedel–de-Häen AG, Seelze-Hannover was used. Acetonitrile (MeCN), *N*-*N*-dimethylformamide (DMF), dimethylsulphoxide (DMSO) and ethanol (EtOH) were obtained from BDH Propylene carbonate (PC), *N*-methylpyrrolidone (*N*-MePy) and *N*-methylformamide (*N*-MF)

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were obtained from Merck (Zur Analyse). The saturated solutions of AgBr in the solvents under consideration were determined gravimetrically as described in previous work [8].

RESULTS AND DISCUSSION

The solubility data [5] of AgBr in the organic solvents, MeCN, *N*-MF, EtOH, DMF, PC, DMSO, *N*-MePy and water are listed in Table 1. The molal solubility was calculated from the molar solubility by dividing the molar values by the densities of the solvents.

From the activity coefficient $\gamma_\pm$ (calculated using the Debye–Hückel equation as explained in ref. 8) and from molal solubility data, values of $\mathrm{p}K_{\mathrm{sp}}$ were estimated by the use of eqn. (1) [9]. These values are also listed in Table 1

$$\mathrm{p}K_{\mathrm{sp}} = -\log S^2 + 2 \log \gamma_\pm \tag{1}$$

The other physical parameters, such as the diameters (σ), densities (d) and dielectric constants (ε) taken from ref. 10 are also reported in Table 1.

The free energies of transfer ($\Delta G_t^\ominus$) of AgBr from water (w) as reference solvent to the organic solvent (s) could be calculated by using $\mathrm{p}K_{\mathrm{sp}}$ values and applying eqn. (2)

$$\Delta G_t^\ominus = 2.303\left[\mathrm{p}K_{\mathrm{sp}}(\mathrm{s}) - \mathrm{p}K_{\mathrm{sp}}(\mathrm{w})\right] \tag{2}$$

The experimental free energies of transfer ($\Delta G_t^\ominus$) of AgBr, expressed as total solvation energies in the solvents under consideration, are presented in Table 1. Their values are divided into neutral (non-electrostatic) free energy of solvation ($\Delta G_t^\ominus(\mathrm{N})$) and electrostatic free energy of solvation ($\Delta G_t^\ominus(\mathrm{el})$)

$$\Delta G_t^\ominus = \Delta G_t^\ominus(\mathrm{N}) + \Delta G_t^\ominus(\mathrm{el}) \tag{3}$$

The electrostatic free energy can be calculated by using the Born equation as follows

$$\Delta G_t^\ominus(\mathrm{el}) = \frac{694.1}{r}\left(\frac{1}{\varepsilon} - 0.012\right) \tag{4}$$

where r is the solvated radius, which is the sum of both the electrolyte and solvent radii. The calculated values of $\Delta G_t^\ominus(\mathrm{N})$ and $\Delta G_t^\ominus(\mathrm{el})$ for AgBr in the organic solvents are also given in Table 1. It was shown from Table 1 that the three types of free energies ($\Delta G_t^\ominus$, $\Delta G_t^\ominus(\mathrm{el})$ and $\Delta G_t^\ominus(\mathrm{N})$) for AgBr have the following order

DMF > EtOH > *N*-MePy > *N*-MF > MeCN > PC > DMSO

For the theoretical calculation of the different solvation free energies, the Pierotti theory [1–3] was applied. This model explains the solvation processes

TABLE 1

Physical properties of organic solvents and solubilities and experimental free energies (in kcal) of AgBr in the organic solvents at 25 ° C

Solvent	Diameter, σ (Å)	Density, d (g cm^{-3})	Dielectric constant, ε	Solubility in molal scale	pK_{sp}	$\Delta G_t^\ominus$	$\Delta G_t^\ominus$ (el)	$\Delta G_t^\ominus$ (N)
MeCN	4.16	0.7768	36	1.262×10^{-3}	21.530	−9.753	0.009	−9.762
N-MF	4.47	0.9998	182.4	5.208×10^{-3}	20.420	−11.266	−0.721	−10.545
EtOH	4.35	0.7851	42.6	8.200×10^{-4}	18.573	−13.786	2.84	−16.626
DMF	4.93	0.9443	36.7	2.503×10^{-3}	16.594	−16.485	1.36	−17.845
PC	5.15	1.1982	64.4	2.630×10^{-3}	21.396	−9.718	0.256	−9.975
DMSO	4.91	1.0950	46.7	2.247×10^{-3}	21.777	−9.416	0.817	−10.234
N-MePy	5.41	0.9308	32	4.889×10^{-3}	20.188	−11.583	1.63	−13.21
H_2O	2.77	0.99707	78.5	7.290×10^{-3}	28.680	0	0	0

TABLE 2

Coefficient Y and the theoretical free energies of the solvation of AgBr in some organic solvents (in kcal at 25 ° C)

Solvent	Y	G_c	ΔG_c	G_L	ΔG_L	G_i	ΔG_i	G_v	ΔG_v	G_{dip}	ΔG_t(dip)	ΔG_{sum}
MeCN	0.94×10^{23}	8.639	−3.401	6.253	0.551	0.159	−0.809	1.574	−0.480	−14.059	−8.581	−12.72
N-MF	0.34×10^{23}	8.202	−3.838	6.586	0.884	0.168	−0.801	1.359	−0.701	−8.786	−3.308	−13.242
EtOH	0.11×10^{23}	8.324	−3.716	6.490	0.788	0.156	−0.813	1.506	−0.554	−18.923	−13.443	−17.738
DMF	1.83×10^{23}	7.368	−4.673	7.332	1.630	0.187	−0.782	1.233	−0.827	–	–	–
PC	2.72×10^{23}	7.096	−4.945	7.613	1.911	0.194	−0.775	1.036	−0.102	−8.995	−3.517	−8.204
DMSO	2.17×10^{23}	7.613	−4.427	7.096	1.394	0.181	−0.787	1.194	−0.866	−6.995	−1.517	−8.991
N-MePy	2.49×10^{23}	6.755	−5.286	7.099	1.398	0.205	−0.764	1.054	−1.006	–	–	–
H_2O	3.60×10^{22}	12.041	0	5.702	0	0.969	0	2.057	0	−5.478	0	0

through the creation of cavities of solute in the solvent followed by interaction. Therefore two different types of free energies are present, cavity and interaction energies, as explained in eqn. (5)

$$\Delta G_t = \Delta G_c + \Delta G_i \tag{5}$$

where ΔG_c is the cavity free energy and ΔG_i is the interaction free energy. The free energy necessary to form a cavity of electrolyte size in solution, was calculated by using Pierotti's theory based on the Reiss model with the knowledge of the hard sphere diameters of solute and solvent molecules. Equation (6) was used for calculation of G_c

$$G_c = -RT\left\{\ln(1-Y) + \left(\frac{3Y}{1-Y}\right)R_{1,2} - \left[\left(\frac{3Y}{1-Y}\right) + \frac{9}{2}\left(\frac{Y}{1-Y}\right)^2\right]R_{1,2}^2\right\} + \frac{NYP}{\rho}R_{1,2}^3 \tag{6}$$

where $Y = (\pi\rho\sigma_1^3)/6$, $\rho = N/V_1^{\ominus}$, N is Avogadro's number, $V_1^{\ominus}$ is the molar volume, $P = 1$ atm, $R_{1,2} = \sigma_2/\sigma_1$, and σ_1 and σ_2 are the hard sphere diameters of the solvent and solute molecules, respectively. The calculated Y (packing density) and G_c values for AgBr obtained using eqn. (5) are represented in Table 2. Values of ΔG_c are calculated by subtracting the cavity free energy value in the organic solvent from that of water. The resulting values are also shown in Table 2.

The interaction free energy (G_i) is a composite of dispersion energy which results from the Lenard Jones 6-12 potential (G_L), the induced free energy (G_{ind}), the volume free energy (G_v) and the dipole–dipole free energy (G_{dip}). The dispersion free energy was evaluated using eqn. (7)

$$G_L = -\tfrac{32}{9}R\pi\rho\sigma_{1,2}^3\sqrt{\frac{\varepsilon_1}{k}\times\frac{\varepsilon_2}{k}} \tag{7}$$

where $\sigma_{1,2} = 1/2(\sigma_1 + \sigma_2)$, $\rho = N/V_1^{\ominus}$ and ε_1/k and ε_2/k are the Lenard Jones energy parameters for organic solvent and solute, respectively. The energy parameters ε_1/k for the solvents used were taken from ref. 11. The ε_2/k value for AgBr was calculated from a semiempirical relation between the bond energies of some known solvents and salts and the Lenard Jones energy parameter and was found to be 134 K. The calculated G_L values for AgBr and their transfer values (ΔG_L) from water to organic solvents are presented in Table 2. The induced free energies (G_{ind}) were calculated from

$$G_{ind} = -\tfrac{12}{9}N\pi\rho\mu_1^2\alpha_2/\sigma_{1,2}^3 \tag{8}$$

where μ_1 is the dipole moment of the solvent [10] and α_2 is the polarizability of the solute. The induced free energies and their transfer values are also given in Table 2. In addition, the volume free energy was calculated by applying eqn. (9) after Lucas and Feillolay [12]

$$G_v = RT \ln \frac{RT}{V} \tag{9}$$

where $V = (x_1 M_1 + x_2 M_2)/d$, x_1 and x_2 are the mole fractions of the solvent and solute, respectively, M_1 and M_2 are the molecular weights of solvent and solute, respectively and d is the density of the pure organic solvent. The estimated values of G_v and ΔG_v for AgBr are also given in Table 2. For further theoretical calculation, the dipole–dipole free energies for the solvation of AgBr with the organic solvents were evaluated by using eqn. (10) [11]

$$G_{\mathrm{dip}} = -\tfrac{8}{9} N \rho \pi \mu_1^2 \mu_2^2 / kT \sigma_{1,2}^3 \tag{10}$$

where μ_1 and μ_2 are the dipole moments of solvent and solute molecules, respectively. The calculated values of G_{dip} and ΔG_{dip} are listed in Table 2.

It is concluded from Tables 1 and 2 that there is a good agreement between the sum of the theoretical free energies of calculation (ΔG_{sum}) and the experimental free energy values ($\Delta G_t^{\ominus}$). It is also shown that the largest contribution to the interaction of AgBr with the organic solvents under consideration comes from the dipole–dipole free energy of solvation.

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