

Thermodynamics of ion-pair association. Part 1. Conductance of sodium tetraphenylborate in 1-alkanols

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Abstract

Conductance measurements are reported for sodium tetraphenylborate (STB) in methanol, ethanol, 1-propanol and 1-butanol at 298.15, 308.15 and 318.15 K. The experimental results were analyzed by the Fuoss–Shedlovsky equation. The limiting conductance Λ_0 and ion-pair association constant $\log K_A$ increase with increasing temperature. Also, the Λ_0 values decrease in the order methanol > ethanol > 1-propanol > 1-butanol; the reverse is true for the $\log K_A$ values. The thermodynamic functions of ion-pair association were evaluated and are discussed. The free energy change of association was found to be linear as a function of the number of methylene groups in the alkyl chain of the 1-alkanols. The thermodynamic parameters of transfer of STB from water to the 1-alkanols were calculated and are discussed.

INTRODUCTION

There is a growing interest in studying solute–solvent interactions. Such interactions are affected by many factors concerning the structures of both solute and solvent. Among them, the dielectric constant, the viscosity, the capability of hydrogen-bond formation and the ionic charge seem to be most important. Comprehensive work by Barthel and co-workers [1–4] on the thermodynamics of ion-pair association, as well as conductivity studies on alkyl ammonium halides and picrates [5–7], bis(2,9-dimethyl-1,10-phenanthroline) copper(I) perchlorate [8] and *S*-alkyl thiuronium halides and picrates [9] in 1-alkanols have revealed the effect of the solvent on the ion-pair association. In addition, Atlani and Justice [10] found that the ion-pair association of STB in hexamethylphosphoramide equals 10.8 M^{-1} , whereas no association was detected in dimethylformamide.

In continuation of our work [11–13] on the influence of the $-\text{CH}_2-$ increment on the thermodynamic functions, the aim of the present report is three-fold: to determine the association behaviour of STB in a homologous series of straight-chain alkanols from conductance measurements at differ-

ent temperatures; to evaluate the thermodynamic parameters of ion-pair association and transfer of STB from water to the alkanols; to correlate the free energy change of association with the number of methylene groups in the alkyl chain of 1-alkanols.

STB was chosen as the studied electrolyte due to the difference in size between the complex and the frequently measured small inorganic ions. Moreover, its charge is screened by bulky phenyl groups. Therefore, one can expect a significant difference in association behaviour [8].

EXPERIMENTAL

Materials

Sodium tetraphenylborate (Merck) was purified according to the method reported by Skinner and Fuoss [14]. Methanol, ethanol, 1-propanol and 1-butanol were dried with Drierite and purified by fractional distillation until their purity, as estimated by gas chromatography, was $\geq 99.8\%$.

Apparatus

Conductance measurements were made on an Electronic Switchgear apparatus, model MC-1. Triplicate measurements were made and the results coincided within 0.2%. Densities were determined by both a weighing bottle and a pycnometer calibrated with deionized water (specific conductance $< 1 \times 10^{-4} \Omega^{-1} \text{m}^{-1}$). Viscosities were measured with a viscometer using deionized water as reference sample. The temperature was adjusted to $\pm 0.01 \text{ K}$ with an ultra-thermostat (Köttermann, 4130, Germany). Each value reported in the tables is the mean of three separate determinations and the maximum error in the density and viscosity measurements was found to be $\leq 0.3\%$. The dielectric constants for methanol, ethanol and 1-propanol were obtained by interpolation from the data of Akerlof [15], and for 1-butanol, interpolation was made from the CRC handbook [16].

RESULTS AND DISCUSSION

The physical properties of pure 1-alkanols (dielectric constants D , viscosities η , and densities ρ) are given in Table 1. It can be seen that there is good agreement between the present values and the literature values.

The conductance measurements of 4×10^{-4} to $10^{-2} \text{ mol l}^{-1}$ sodium tetraphenylborate (STB) in methanol, ethanol, 1-propanol and 1-butanol were carried out at 298.15, 308.15 and 318.15 K.

The Debye–Hückel–Onsager equation was applied in plotting the equivalent conductance Λ against its specific molar concentration $C^{1/2}$, and a preliminary value for the limiting conductance or the equivalent conduc-

TABLE 1

Physical properties of 1-alkanols at different temperatures

Temp./K	Methanol	Ethanol	1-Propanol	1-Butanol
$\rho/\text{g ml}^{-1}$				
298.15	0.78662	0.78501	0.79975	0.80559
	0.78658 ^a	0.78511 ^b	0.79960 ^b	0.80576 ^c
308.15	0.77776	0.77713	0.79129	0.79813
318.15	0.76840	0.76848	0.78320	0.79051
$10^3\eta/\text{Pa s}$				
298.15	0.5431	1.0859	1.9427	2.5860
	0.5445 ^a	1.0840 ^b	1.9430 ^d	2.5870 ^e
308.15	0.4839	0.8657	1.5693	2.2131
318.15	0.4351	0.7014	1.2893	1.5843
D				
298.15	31.50	24.30	20.18	17.10
	32.62 ^a	24.33 ^b	20.45 ^b	17.45 ^c
308.15	29.86	22.90	18.90	15.70
318.15	28.24	21.50	17.68	14.40

^a Ref. 5. ^b Ref. 6. ^c Ref. 7. ^d Ref. 17. ^e Ref. 9.

tance at infinite dilution Λ_0 was obtained by free extrapolation to zero concentration.

The ion-pair dissociation constants K_d can, in principle, be calculated from the relation

$$K_d = \frac{C\alpha^2 f_{\pm}^2}{1 - \alpha} = \frac{1}{K_A} \quad (1)$$

where K_A is the ion-pair association constant, f_{\pm} is the activity coefficient of the electrolyte, and α is the degree of dissociation which is related to Λ_0 through the relation

$$\alpha = \frac{\Lambda S(z)}{\Lambda_0} \quad (2)$$

Accurate Λ_0 values should be available in order to apply eqns. (1) and (2). Thus it is more reliable and applicable to use another approach which yields both Λ_0 and K_A simultaneously. For that, the Fuoss and Shedlovsky equation [18] was applied

$$\frac{1}{\Lambda S(z)} = \frac{1}{\Lambda_0} + \frac{C\Lambda f_{\pm}^2 S(z)K_A}{\Lambda_0^2} \quad (3)$$

The Shedlovsky function $S(z)$ was recorded by Daggett [19] and defined as

$$S(z) = \{z/2 + [1 + (z/2)^2]^{1/2}\}^2$$

where z is calculated from

$$z = S\Lambda_0^{-3/2}(C\Lambda)^{1/2}$$

and S is the Onsager slope, defined as

$$S = a\Lambda_0 + b$$

in which $a = 0.8204 \times 10^6/(DT)^{3/2}$, $b = 82.50/\eta(DT)^{1/2}$ and η is the viscosity of the alcohol.

The association constants of STB in different alcohols have been evaluated using eqn. (3). By plotting $1/\Lambda S(z)$ versus $C\Lambda f_{\pm}^2 S(z)$, a straight line is obtained, the slope of which equals K_A/Λ_0^2 , with the intercept $1/\Lambda_0$. Therefore, more accurate values are obtained for the association constants K_A and for Λ_0 .

Table 2 lists $\log K_A$ and Λ_0 values at different temperatures. Inspection of these values reveals that:

(i) At constant temperature, the Λ_0 values decrease with decreasing dielectric constant D in the order: methanol > ethanol > 1-propanol > 1-butanol. This may be due to the decrease in the ionic mobility with a decrease in D . Similar results were obtained for alkyl ammonium halides and picrates [5–7], bis(2,9-dimethyl-1,10-phenanthroline) copper(I) perchlorate [8] and S -alkyl thiuronium halides and picrates [9] in 1-alkanols.

TABLE 2

Limiting conductance Λ_0 and ion-pair association constant $\log K_A$ at different temperatures for sodium tetraphenylborate and the corresponding thermodynamic parameters

Property	Temp./K	Methanol	Ethanol	1-Propanol	1-Butanol
$10^4\Lambda_0/$ ($\Omega^{-1} \text{ m}^2 \text{ mol}^{-1}$)	298.15	63.10	37.52	21.41	8.55
	308.15	72.44	45.90	25.72	11.20
	318.15	81.28	54.61	33.01	13.58
Walden product	298.15	0.342	0.407	0.416	0.221
	308.15	0.351	0.397	0.404	0.248
	318.15	0.354	0.383	0.426	0.215
$\log K_A$	298.15	1.55	1.74	1.92	2.11
	308.15	1.62	1.81	2.01	2.20
	318.15	1.67	1.91	2.10	2.30
$-\Delta_{\text{ass}}G^\circ/(\text{kJ mol}^{-1})$	298.15	8.85	9.93	10.99	12.05
	308.15	9.56	10.68	11.83	12.98
	318.15	10.17	11.64	12.79	14.01
$\Delta_{\text{ass}}H^\circ \text{ }^a/(\text{kJ mol}^{-1})$	308.15	10.91	15.40	16.34	17.24
$\Delta_{\text{ass}}S^\circ/(\text{J K}^{-1} \text{ mol}^{-1})$	308.15	66.3	84.9	91.6	98.2
$\Delta_{\text{ass}}H^\circ \text{ }^b/(\text{kJ mol}^{-1})$	308.15	9.99	14.81	17.04	18.27

^a Calculated from $\log K_A$ vs. $1/T$. ^b Calculated from $\log \Lambda_0$ vs. $1/T$.

(ii) For each alcohol, Λ_0 increases with increasing temperature. This can be explained as follows: the increase in temperature causes a decrease in the viscosity of the solvent (Table 1) which in turn leads to an increase in ionic mobility and a decrease in frictional forces. Kay et al. [5] obtained similar results for tetraalkyl ammonium halides and picrates in methanol. It can be seen from Table 2 that the Walden products of STB in 1-alkanols are temperature independent, revealing that the conductance mechanism for these systems at infinite dilution is viscosity dependent.

(iii) At constant temperature, $\log K_A$ increases non-linearly with $1/D$. Although the plot of $\log K_A$ versus $1/D$ is expected to be linear according to Fuoss (eqn. (4)), curvature is observed (Fig. 1). The non-linearity reveals the existence of a strong interaction between the solvent and the electrolyte. Similar results were obtained by Hafez et al. [9] and Evans and Gardam [7]

$$K_A = \frac{4\pi Na^3}{3000} \exp \frac{Z_+ Z_- e_0^2}{DkT} \quad (4)$$

(iv) For each alcohol, $\log K_A$ increases with increasing temperature. Similar trends were observed for tetraalkylammonium bromides in methanol [5], tetraalkylammonium picrate in three alkyl solvents [20] and

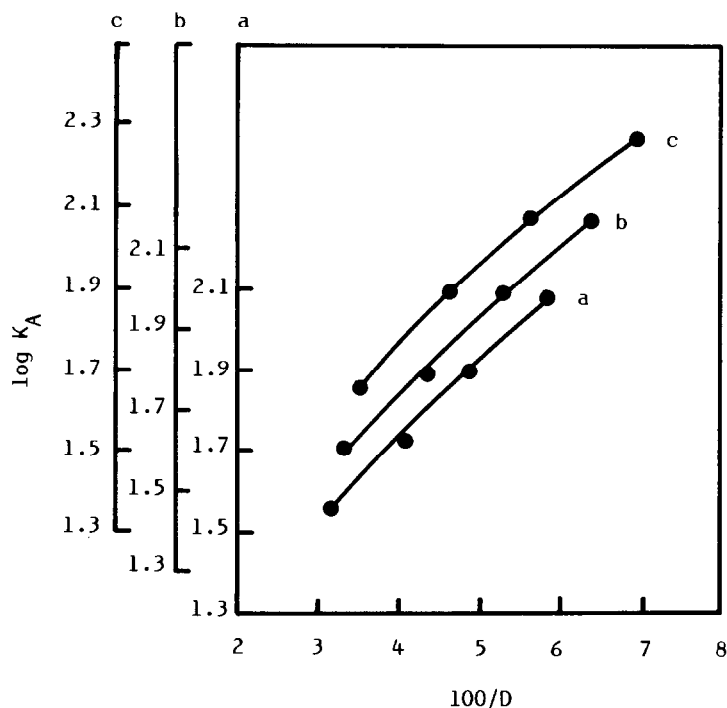


Fig. 1. Dielectric constant dependence of the association constant of sodium tetraphenylborate in 1-alkanols at a, 298.15 K; b, 308.15 K; and c, 318.15 K.

substituted phenyltrimethylammonium perchlorate in ethylene chloride and ethylidene chloride [21]. Kay et al. [5] attributed the decrease in association with decreasing temperature to the change in the DT product.

Thermodynamics of ion-pair association

The free energy changes $\Delta_{\text{ass}}G^\ominus$ of ion-pair association were calculated by applying the relationship

$$\Delta_{\text{ass}}G^\ominus = -RT \ln K_A$$

For STB in each alcohol, the plot of $\Delta_{\text{ass}}G^\ominus$ values, as ordinates, versus T , as abscissae, did not deviate from the most probable straight line by more than the experimental error (the regression coefficients were close to 1). Therefore, $\Delta_{\text{ass}}H^\ominus$ and $\Delta_{\text{ass}}S^\ominus$ have constant values over the temperature range 298.15–318.15 K. Thus, the following equation is valid

$$\Delta_{\text{ass}}G^\ominus = \Delta_{\text{ass}}H^\ominus - T\Delta_{\text{ass}}S^\ominus$$

in which the enthalpy changes $\Delta_{\text{ass}}H^\ominus$ were calculated from the slopes of the plots of $\log K_A$ versus $1/T$ (Fig. 2).

The obtained thermodynamic functions of ion-pair association are listed in Table 2. Inspection of these values reveals that both the enthalpy and entropy values are positive while the free energy change values are negative. Similar results were obtained by Denison and Ramsey [21]: they obtained negative values for enthalpy and entropy changes and positive values for free energy changes of ion-pair dissociation. The decrease in entropy of dissociation was interpreted [21] to indicate that the decrease in entropy of

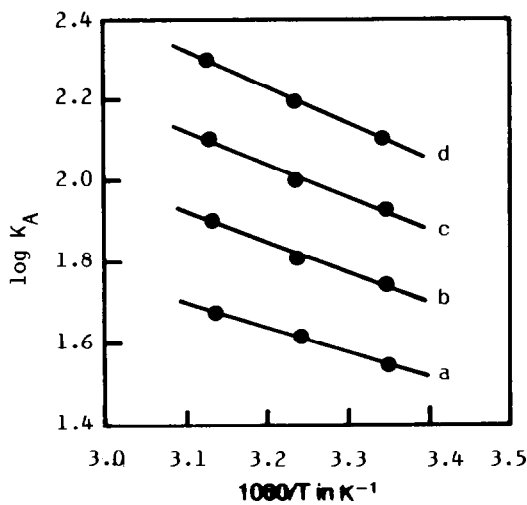


Fig. 2. Temperature dependence of the association constants: plots of $\log K_A$ of sodium tetraphenylborate versus $1/T$ in a, methanol; b, ethanol; c, 1-propanol; and d, 1-butanol.

the solvent, due to the greater ordering of the solvent molecules by the free ions (relative to that by the associated ion-pairs), exceeds the increase in entropy accompanying the dissociation of the unsolvated ion-pair into free unsolvated ions.

The positive $\Delta_{\text{ass}}H^\circ$ values reveal that the solvated ion-pair represents a less stable arrangement than the solvated ions, i.e. the ion-pair–solvent bond is weaker than the ion–solvent bond.

Applying eqn. (5) derived by Ritzoulis et al. [22], $\Delta_{\text{ass}}H^\circ$ values can also be calculated

$$\log \Lambda_0 + \frac{2}{3} \log \rho = -\frac{\Delta_{\text{ass}}H^\circ}{2.303RT} + C \quad (5)$$

where ρ is the density of the electrolyte solution and C an integration constant.

Therefore, the slope of the graph of $\log \Lambda_0$ versus $1/T$ was utilized to estimate $\Delta_{\text{ass}}H^\circ$, where the term $(2/3)\log \rho$ is very small and almost constant. The derived $\Delta_{\text{ass}}H^\circ$ values are listed in Table 2. As can be seen, there is good agreement, within the approximation made and the experimental error, between those $\Delta_{\text{ass}}H^\circ$ values and the corresponding values derived from the $\log K$ versus $1/T$ plot.

Constancy of CH_2 increment

Figure 3 shows $-\Delta_{\text{ass}}G^\circ$ values of STB at different temperatures plotted against the number of methylene groups N_{CH_2} in the alkyl chain of 1-alkanols. By linear regression (regression coefficient ≈ 1) of the data in Fig. 3, the following relations are obtained at 298.15, 308.15 and 318.15 K, respectively: $-\Delta_{\text{ass}}G^\circ(298.15 \text{ K}) = 7.79 + 1.07N_{\text{CH}_2}$, $-\Delta_{\text{ass}}G^\circ(308.15 \text{ K}) = 8.41 + 1.14N_{\text{CH}_2}$, and $-\Delta_{\text{ass}}G^\circ(318.15 \text{ K}) = 8.99 + 1.27N_{\text{CH}_2}$.

It is clear that there is a constant increase in the value of $-\Delta_{\text{ass}}G^\circ$ with the number of methylene groups, indicating that the hydrophobicity of the 1-alkanols plays an important role in the association of STB. Thus, extrapolation of the lines to $N_{\text{CH}_2} = 0$ yields intercept values of 7.79, 8.41 and 8.99 kJ mol^{-1} at 298.15, 308.15 and 318.15 K, respectively, corresponding to the $-\Delta_{\text{ass}}G^\circ$ values of STB in water. Moreover, the corresponding $\Delta_{\text{ass}}H^\circ$ and $\Delta_{\text{ass}}S^\circ$ values of STB in water were found to be 10 kJ mol^{-1} and 60 $\text{J K}^{-1} \text{ mol}^{-1}$, respectively. Therefore, the present correlation method is of utmost importance, particularly for compounds which are not easily soluble in water, such as STB.

Thermodynamics of transfer

The free energy change of transfer of STB from water, as a reference solvent, to 1-alkanols were calculated from the relation [23]

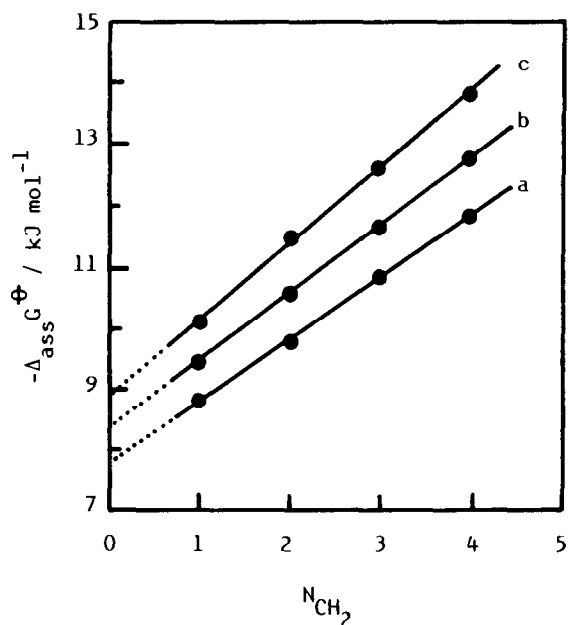


Fig. 3. Association free energy change $-\Delta_{\text{ass}}G^{\circ}$ of sodium tetraphenylborate versus the number of methylene groups in the alkyl chain of 1-alkanols at a, 298.15 K; b, 308.15 K; and c, 318.15 K.

$$\Delta_{\text{w}}^{\text{al}}G = -2.303RT\Delta\log K_{\text{A}}$$

or

$$\Delta_{\text{w}}^{\text{al}}G = \Delta_{\text{ass}}G^{\circ}(\text{alkanol}) - \Delta_{\text{ass}}G^{\circ}(\text{water})$$

where $\Delta\log K_{\text{A}}$ is the difference between the association constant of STB in 1-alkanol and water, respectively.

The calculated values of $\Delta_{\text{w}}^{\text{al}}G$ are listed in Table 3. Inspection of the values in Table 3 reveals the following:

(i) The hydrophobicity of the solvents is among the factors which may explain the association of STB in 1-alkanols.

TABLE 3

Thermodynamics of transfer of sodium tetraphenylborate from water to 1-alkanols

Solvent	$-\Delta_{\text{w}}^{\text{al}}G/(\text{kJ mol}^{-1})$			$\Delta_{\text{w}}^{\text{al}}H/(\text{kJ mol}^{-1})$	$\Delta_{\text{w}}^{\text{al}}S/(\text{J K}^{-1} \text{mol}^{-1})$
	298.15 K	308.15 K	318.15 K	308.15 K	308.15 K
Methanol	1.06	1.15	1.18	0.91	6.5
Ethanol	2.14	2.27	2.65	5.40	25.1
1-Propanol	3.20	3.42	3.80	16.34	31.8
1-Butanol	4.26	4.57	5.02	17.24	38.4

(ii) All $\Delta_w^{\text{al}}G$ values are negative, indicating that in the present case 1-alkanols are more favourable solvents than water.

(iii) The transfer thermodynamic parameters, $\Delta_w^{\text{al}}G$, $\Delta_w^{\text{al}}H$ and $\Delta_w^{\text{al}}S$ values increase on going from methanol to 1-butanol. This may be attributed to the increase in the interaction of STB with 1-alkanols which follows the same order as a result of the increase in the hydrophobicity of the studied 1-alkanols.

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