revealed as sharply increased η_{sp}, also take place cooperatively at narrow pH range, 4.7 for Cu^{2+} and 6.2 for Ni^{2+}. The absence of abrupt η_{sp} change for Mg^{2+} indicates that the metal ion does not bind to chitosan in the experimental pH range. Other metal ions which form amine complexes are expected to chelate to chitosan at appropriate pH's. However, precipitation of chitosan and metal hydroxides at higher pH prevented the study. The difference in chelating properties among metal ions suggests that separation of a mixture of metal ions into its components is possible by ion chromatography or dialysis using chitosan gel matrix with variation of pH of eluent or medium. The chitosan gel suitable for this purpose can be prepared by partial N-acylation[12].

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The Pressure Effect on the Ionic Association of the 3, 5, N-trimethyl Pyridinium Iodide in Ethanol-Water Mixture

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The association constants (K) of 3,5,N-trimethyl pyridinium iodide in 95 volume percent ethanol-water mixed solvent were determined by a modified UV and conductance method at 25°, 30°, 40° and 50°C over the pressure range 1 to 2000 bars. The association process is enhanced with increasing pressure and decreasing temperature. From K values, we obtained the total partial molar volume change (ΔV) and some thermodynamic parameters. The electrostriction volume (ΔV_{el}) and intrinsic volume (ΔV_{in}) were also evaluated. The values of ΔV, ΔV_{el}, ΔV_{in} are negative, negative and positive, respectively, and the absolute values of all these three decrease with increasing pressure and temperature. The ion-pair size (a) were varied 3 to 6 Å with pressure and temperature. The solvation number (n) decreased from 2 to 0.5 with increasing temperature.

Introduction

In 1955, Kosower[1,2] showed that N-methyl pyridinium iodide (NMPI) made an ultraviolet charge transfer band in solution. This band supposedly arises due to the transfer of electron density from the highest occupied orbital of iodide to the lowest unoccupied orbital of the N-methyl pyridinium cation.

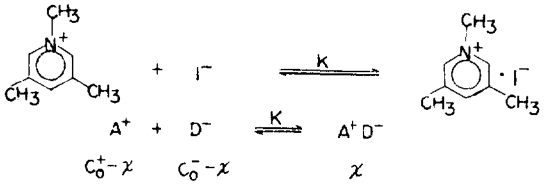
Recently, the thermodynamic investigation of the association process of NMPI in ethanol-water mixture was discussed by Paul Hemmes *et al.*[3]

Hitherto few pressure studies have been undertaken to analyze the electrostatic aspects of the dissociation process of ion pairs.[4,5,6]

We studied the pressure effect on the association of 2, N-dimethyl pyridinium iodide in 95 volume percent ethanol-water mixed solvent in the previous paper.[7]

In this report, we want to discuss the pressure dependence of the ionic association process of 3,5,N-trimethyl pyridinium iodide (TMPI) in the same solvent mentioned above.

The ionic equilibrium relationship of the 3,5,N-trimethyl pyridinium iodide can be expressed by eq. (1).



(1)

In this formula, cation accepts electron from anion and form dipolar ionic complex, where A^+, D^- and A^+D^- represent 3,5,N-trimethyl pyridinium cation, iodic anion and 3,5,N-trimethyl pyridinium iodide, respectively. C_0^+, C_0^- are the initial cation and anion concentration, respectively and x the concentration of ionic complex.

The equilibrium relationship of the above equation can be formulated as following

$$K=\frac{x}{(C_0^+-x)(C_0^--x)} \tag{2}$$

We modified eq. (2) by multiplying Shedlovsky function S which was expressed in the previous paper.[8,9] Replacing x by A/ϵ and putting $C_0^+=C_0^-=C_0$ then we obtain the next equation.

$$\frac{C_0^2S}{A}=\frac{(2C_0-x)S}{\epsilon}+\frac{1}{K\epsilon} \tag{3}$$

The equilibrium molar concentration of ionic complex x can be defined by

$$x=C_0(1-\gamma) \tag{4}$$

where γ, the degree of dissociation of eq. (1) is defined in nonaqueous system[8] by

$$\gamma=\frac{\Lambda}{\Lambda_0}S \tag{5}$$

Using the relation of eq. (4) and $x=A/\epsilon$

$$\epsilon=\frac{A}{C_0-\gamma C_0} \tag{6}$$

We obtained more refined form of γ by replacing the concentration C_0 with the activity fC_0 in eq. (4).

$$\gamma=\frac{(fC_0-A/\epsilon)}{fC_0} \tag{7}$$

where f is the activity coefficient.

Substituting eq. (4) into eq. (3) and replacing C_0 with fC_0, we obtain the following relationship

$$\frac{(fC_0)^2S}{A}=\frac{1}{\epsilon}[(1+\gamma)fC_0S]+\frac{1}{K\epsilon} \tag{8}$$

We calculated the corrected ϵ, f, γ, K values by successive cyclic interations from eq. (5) to eq. (8) using the computer program until $|\epsilon_i-\epsilon_{i+1}|/\epsilon\leq 0.05$ reached.

Experimental

Chemicals. TMPI, synthesized from 3,5-dimethyl pyridine and methyl iodide refluxed in absolute ethanol, was twice recrystallized from absolute ethanol to give white crystals(mp:260°C). After drying, TMPI was stored in a desiccator over $CaCl_2$.

Preparation of Stock Solution. Stock solution was prepared by dissolving weighed sample of TMPI in the 95 % ethanol-water mixture. The solutions for the measurement were prepared in the concentration range of 1×10^{-4} $\sim5\times10^{-4}$ M by diluting the stock solution with the same solvent at room temperature.

Apparatus and Measurements. The conductivity cell, the high pressure apparatus and the method of applying pressure were already described in previous paper.[7,10] The conductometric measurements were carried out at 25°, 30°, 40°, 50°C(±0.01°C) over a pressure range up to 2000 bars using conductivity bridge (♯ PM-70 CB, Barnstead Sybron Co) and the absorbancy was measured with double beam spectrophotometer (SHIMADZU-210A). The observed λ_{max} of TMPI in 95 % ethanol-water mixture was 272 nm at atmospheric pressure.

Results and Discussion

From the values of conductivity measured, we obtained the equivalent conductance (Λ) at various pressures and temperatures. An increase of the equivalent conductance with pressure and temperature is clearly shown from the conductance data plotted in Figure 1, Figure 2, Figure 3 and Figure 4. The limiting equivalent conductances (Λ_0) were obtained by extrapolating these plots to zero concentration and the values were listed in Table 1.

Dielectric constants[11,12] and viscosities[13] of the ethanol-water mixed solvent were calculated in the ratio of volume percentage using the data taken from the literature. The data for the solvent composition were given in the previous paper.[7]

The method of computation presented above has been applied to a number of conductance data and we evaluated the values of molar extinction coefficients (ϵ), activity coefficients (f), degree of dissociation (γ), association constants (K) of TMPI in 95% ethanol-water mixed solvent. By the way, the density of ethanol-water mixed solvent varies with pressure, but the change of concentration with pressure is within the range of experimental error because the solution is very dilute. So we used mole concentration.

The results were summarized in Table 2, Table 3, Table 4 and Table 5. From the tabulated data, we know that the association constants of each ion-pair increase with increasing pressure and decrease with increasing temperature. For the degree of dissociation, the reverse trend is shown.

The fundamental equation for the effect of pressure on the equilibrium constant of a reaction is

$$\left(\frac{\partial \ln K}{\partial P}\right)_T=-\frac{\Delta V}{RT} \tag{9}$$

The pressure dependence of the association constants was illustrated in Figure 5. We put the functional dependence of ln K upon pressure as parabolic

$$\ln K=a+bP+cP^2 \tag{10}$$

The functional constants of eq. (10) were calculated by the

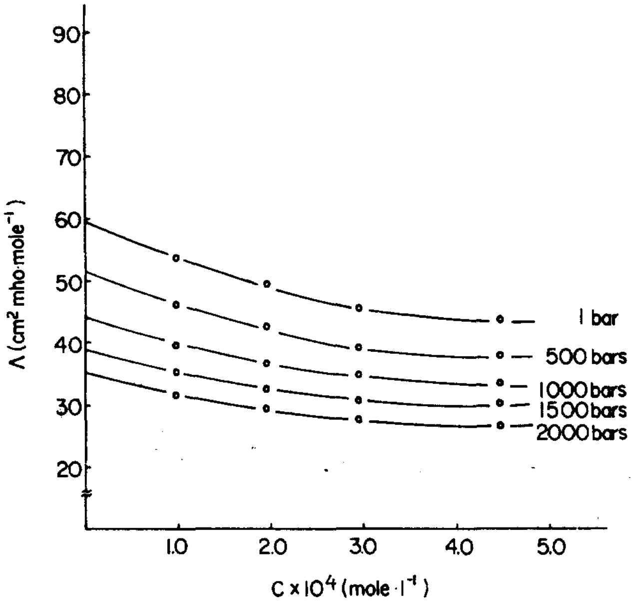
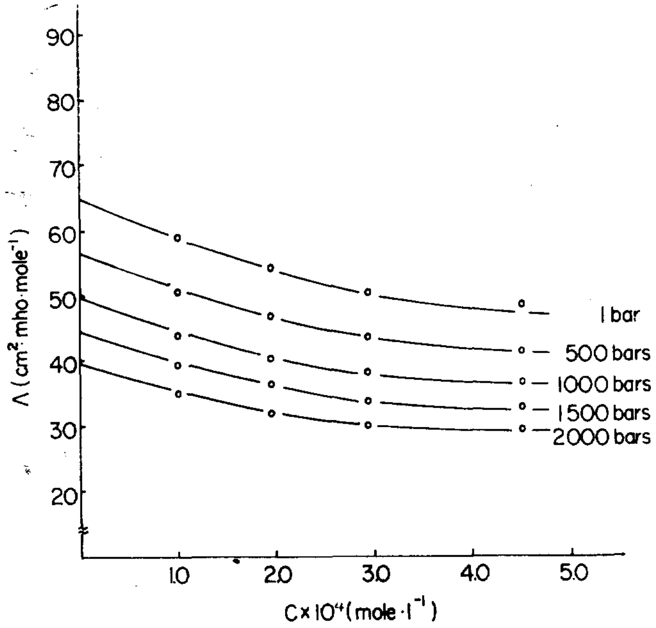


Figure 1. The plot of Λ *vs. C* for TMPI in 95 % ethanol–water mixture at 25 °C.



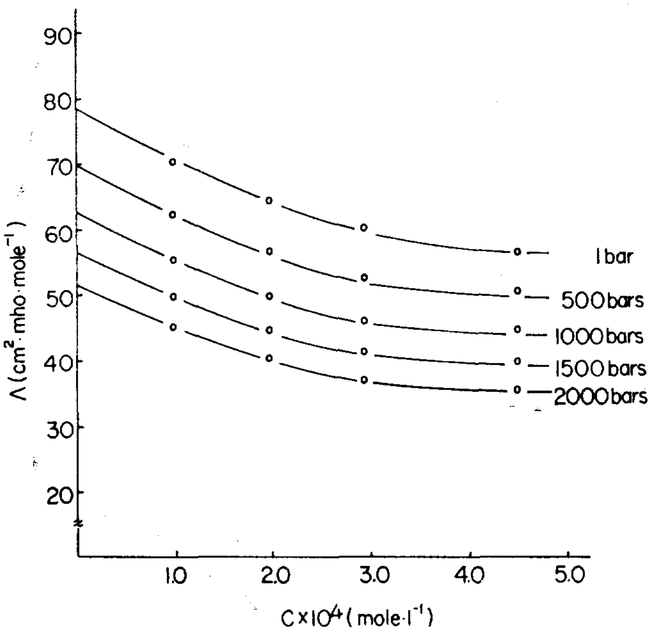
Figuer 2. The plot of Λ *vs. C* for TMPI in 95 % ethanol–water mixture at 30 °*C*.

TABLE 1: Limiting Equivalent Conductances (Λ_0 cm². mho. mole⁻¹) of TMPI in 95 % Ethanol-Water Mixture

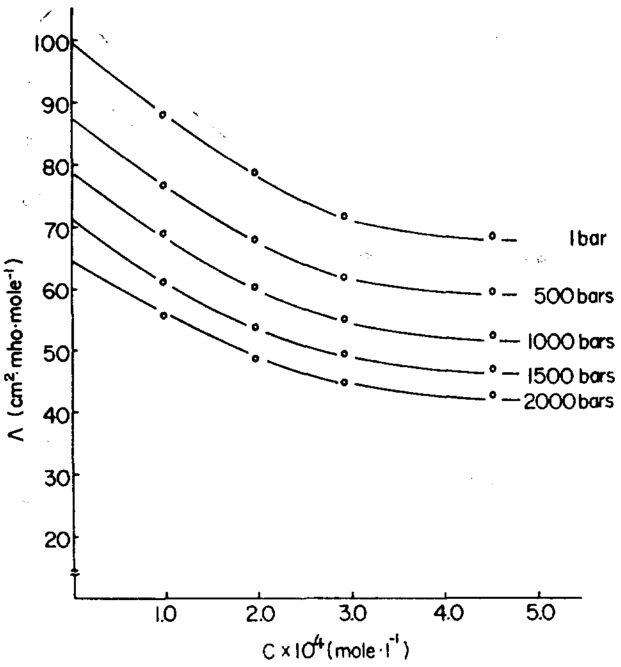
T (°C)	P (bars)				
	1	500	1000	1500	2000
25	59.5	51.1	44.5	38.7	34.9
30	65.1	56.5	49.7	43.6	39.4
40	79.0	69.6	63.5	56.3	51.5
50	99.5	87.3	78.5	70.7	64.2

least squares method and were given in Table 6. Substituting eq. (10) into eq. (9), we obtain the following equation for the evaluation of ΔV.

$$\Delta V = -RT(b+2cP) \qquad (11)$$



Figuer 3. The plot of Λ *vs. C* for TMPI in 95 % ethanol–water mixture at 40 °C.



Figuer 4. The plot of Λ *vs. C* for TMPI in 95 % ethanol–water mixture at 50 °C.

TABLE 2: Molar Extinction Coefficients ($\epsilon \times 10^{-4}$ l·mole⁻¹·cm⁻¹) of TMPI

T (°C)	P (bars)				
	1	500	1000	1500	2000
25	1.50	1.45	1.42	1.40	1.39
30	1.96	1.72	1.61	1.58	1.54
40	2.02	1.97	1.93	1.91	1.89
50	2.17	2.10	2.01	1.95	1.89

The volume change accompaning the association of the ion-pairs, ΔV was calculated from the above equation and the

TABLE 3: Activity Coefficients (f) of TMPI

$C\times10^4$ (mole·l^{-1})	T(°C)	P(bars)				
		1	500	1000	1500	2000
4.50	25	0.930	0.934	0.937	0.938	0.940
	30	0.928	0.934	0.937	0.938	0.940
	40	0.925	0.932	0.937	0.938	0.940
	50	0.924	0.932	0.937	0.938	0.941
2.93	25	0.941	0.945	0.947	0.948	0.951
1.95	25	0.948	0.952	0.954	0.956	0.957
0.98	25	0.962	0.964	0.966	0.967	0.968

TABLE 4: Degree of Dissociation (γ) of TMPI

$C\times10^4$ (mole·l^{-1})	T (°C)	P (bars)				
		1	500	1000	1500	2000
4.50	25	0.580	0.577	0.567	0.566	0.565
	30	0.654	0.641	0.630	0.619	0.605
	40	0.696	0.693	0.682	0.676	0.652
	50	0.708	0.701	0.686	0.678	0.665
2.93	25	0.648	0.635	0.627	0.623	0.621
1.95	25	0.753	0.733	0.732	0.715	0.706
0.98	25	0.879	0.876	0.872	0.861	0.857

TABLE 5: Association Constants ($K\times10^{-3}$ l·mole^{-1}) of TMPI

T (°C)	P (bars)				
	1	500	1000	1500	1000
25	2.89	3.39	3.94	4.54	5.22
30	2.12	2.57	2.83	3.10	3.71
40	1.70	1.86	2.04	2.14	2.37
50	1.38	1.51	1.59	1.67	1.82

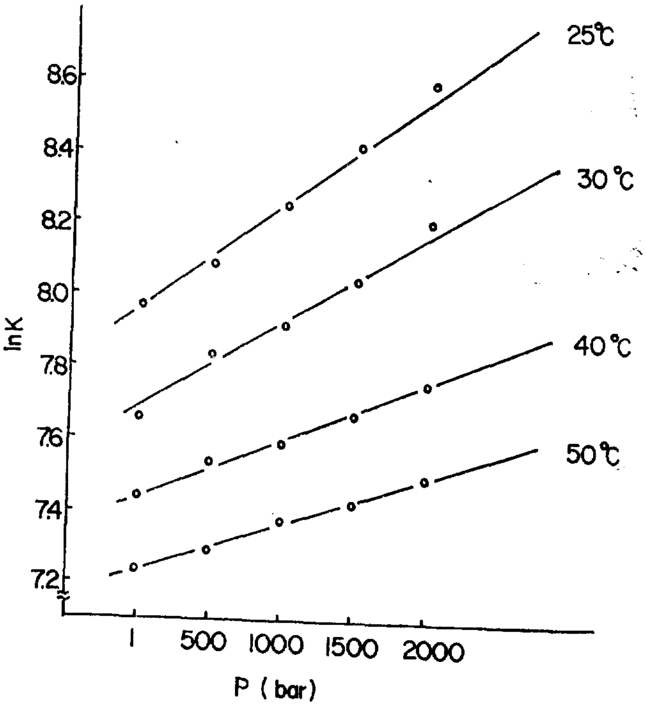
TABLE 6: The Coefficients of Eq. (10) for the Function of ln K with respect to P

T (°C)	a	b×10⁴	c×10⁸
25	7.9706	3.2307	−14.4680
30	7.6775	2.7949	−8.6905
40	7.4430	1.7168	−5.8051
50	7.2379	1.3216	−0.0572

results were listed in Table 7. Moreover ΔV, the partial molar volume change, would be the sum of two major components, that is,

$$\begin{aligned}\Delta V &= \Delta V_{\text{el}} + \Delta V_{\text{in}} \\ &= [V_{\text{A}^+\text{D}^-} - (V_{\text{A}^+} + V_{\text{D}^-})] - n(V_0 - V) \qquad (12)\end{aligned}$$

where ΔV_{in} is the intrinsic partial molar volume change and ΔV_{el} is the electrostriction partial molar volume change. And $V_{\text{A}^+\text{D}^-}$, V_{A^+}, V_{D^-}-are molar volumes of the corresponding species, respectively, n the number of solvent molecules incorporated with TMPI V_0 molar volume of solvent, V molar volume of compressed solvent due to solvation. Electrostriction volume is due to the contraction of solvent in the field of ions and it counterbalances the contribution of the intrinsic volume due to the reacting particle themselves, so that they actually have net negative total partial molar volumes in solutions.



Figuer 5. The plot of ln K vs. P for TMPI.

In order to evaluate ΔV_{el}, we used the equation obtained by Jacques Everaert and Andre Persoons[6] which was derived from Born's formula[14] for the ionic association process

$$\Delta V_{\text{el}} = -\frac{Ne^2}{aD^2}\left(\frac{\partial D}{\partial P}\right)_T + \left(\frac{3RT}{a} - \frac{Ne^2}{a^2D}\right)\left(\frac{\partial a}{\partial P}\right)_T \qquad (13)$$

where N, e and R are Avogadro number, electronic charge and universal gas constant, respectively, D dielectric constant of solvent, a the ion-pair size. Hamann *et al*[15-17] showed another expression for ΔV from Fuoss's theory[18] of ion-pair formation

$$\Delta V = \frac{N|z_1z_2|e^2}{a}\left(\frac{\partial D^{-1}}{\partial P}\right)_T + RT\left(\frac{\partial \ln \rho}{\partial P}\right)_T \qquad (14)$$

where ρ is the density of the mixed solvent calculated to the mole ratio of ethanol[11,12] and water[19] from the literature data.

Using the ΔV values evaluated above, we can estimate the ion-pair size (a) from eq. (14) and listed the data in Table 8. Using the values of ion-pair size (a) evaluated above, we can obtain ΔV_{el} and ΔV_{in} from eq. (12) and eq. (13). These values are shown in Table 9. The values of ΔV_{el} are negative and the values of ΔV_{in} are positive. The absolute values of these two decrease with increasing pressure and temperature. Differentiating eq. (12) with respect to V_0 assuming that n and V are independent of applied pressure over the pressure range employed, we obtain the following equation.

$$\left(\frac{\partial \Delta V}{\partial V_0}\right)_T = \left(\frac{\partial \Delta V_{\text{in}}}{\partial P}\right)_T \left(\frac{\partial P}{\partial V_0}\right) - n \qquad (15)$$

Examining the values of solvation number (n) given in Table 8, we can say that about two molecules of solvent incorporated with TMPI at 25°C and almost dehydrate at 50°C.

The other thermodynamic parameters associated with the ionic association constants (K) of eq. (1) are given by the

TABLE 7: Total Partial Molar Volume Change ($-\Delta V$ cm^3·mole^{-1}) of TMPI

T (°C)	P (bars)				
	1	500	1000	1500	2000
25	7.90	7.55	7.20	6.84	6.49
30	6.95	6.74	6.52	6.30	6.09
40	4.41	4.26	4.11	3.96	3.81
50	3.50	3.50	3.50	3.50	3.50

TABLE 8: Ion-pair Size ($a\times10^8$ cm) and Solvation Number (n) of TMPI

	T (°C)	P (bars)				
		1	500	1000	1500	2000
a	25	3.06	3.18	3.31	3.45	3.60
	30	3.39	3.48	3.57	3.68	3.78
	40	4.81	4.93	5.06	5.20	5.34
	50	5.61	5.61	5.61	5.61	5.61
n	T (°C)	25	30	40	50	
		1.90	1.26	0.93	0.55	

TABLE 9: The Intrinsic Volume Change (ΔV_{in} cm^3·mole^{-1}) and the Electrostriction Volume Change ($-\Delta V_{el}$ cm^3·mole^{-1}) of TMPI

	T (°C)	P (bars)				
		1	500	1000	1500	2000
ΔV_{in}	25	17.21	14.50	13.63	11.15	9.82
	50	4.64	3.65	3.07	2.84	2.52
$-\Delta V_{el}$	25	25.11	22.05	19.83	17.99	16.31
	50	8.14	7.15	6.57	6.34	6.02

TABLE 10: Thermodynamic Parametrs of TMPI at 30°C and Various Pressures

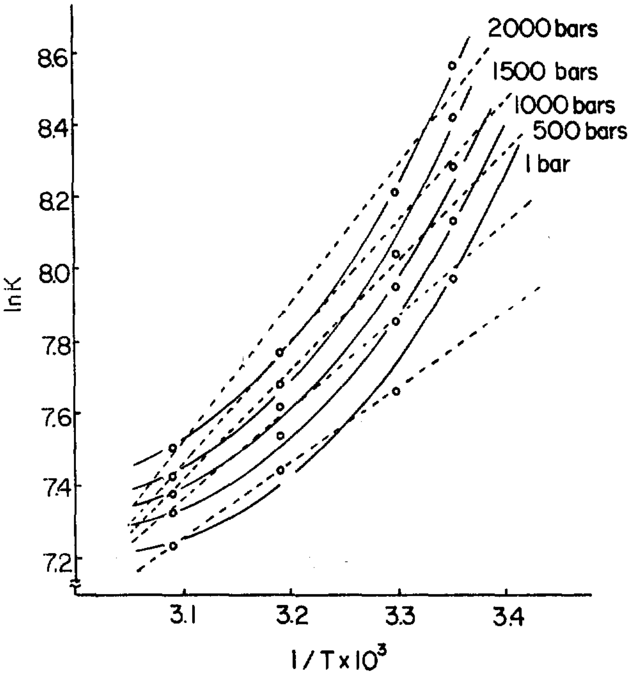
P (bars)	1	500	1000	1500	2000
ΔG° (kcal·mole^{-1})	−4.61	−4.73	−4.79	−4.84	−4.95
ΔH° (kcal·mole^{-1})	−4.11	−4.83	−5.37	−5.76	−6.86
ΔS° (e.u.)	1.65	−0.33	−1.91	−3.03	−6.30

$$\Delta G^\circ = -RT\ln K \qquad (16)$$

$$\Delta H^\circ = -R\left(\partial \ln K/\partial\left(\frac{1}{T}\right)\right)_P \qquad (17)$$

$$\Delta S^\circ = \frac{1}{T}(\Delta H^\circ - \Delta G^\circ) \qquad (18)$$

plots of. lnk. *vs.* (1/T) under various pressures are illustrated in Figure 6.The calculated values of the standard free energy change (ΔG°), the standard enthalpy change (ΔH°), and the standard entropy change (ΔS°) were shown in Table 10. From the results, we know that this ion-pair association reaction is exothermic and the ion-pair is more stable at high pressure. The value of ΔS° is positive at 1 bar and negative above 500 bars. There are two factors that control entropy of the reaction system. One is entropy decreasing factor due to ion-pair formation and the other is entropy increasing factor due to dehydration. At 1 bar, the former prevails. As pressure increases, the quantity of free solvent is reduced and the entropy of the system decreases. The extent of hydration of the ion-pairs correlates with the values of ΔS° in the association process of TMPI.



Figuer 6. The plot of ln K *vs.* (1/T) for TMPI.

Generally, solvation of an ion-pair is less than the solvation of a free ion, therefore as ion-pair association process occurrs, the electrostriction volume is reduced and the absolute values of ΔV_{el} decrease with increasing pressure because the degree of dehydration becomes smaller at high pressure, that is, the difference of volumes in free ion state and activated complex state due to solvation is small at high pressure ion-pair state.

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Crystal Structure of Dehydrated Cesium and Silver Exchanged Zeolite A, $Cs_{7.3}Ag_{4.7}$–A

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The structure of $Cs_{7.3}Ag_{4.7}Si_{12}Al_{12}O_{48}$, vacuum dehydrated zeolite A with all Na^+ ions replaced by Cs^+ and Ag^+ as indicated, has been determined by single–crystal x–ray diffraction techniques in the cubic space group, *Pm3m* (a = 12.282 (1) Å). The structure was refined to the final error indices $R_1 = 0.089$ and R_2 (weighted) $= 0.099$ using 347 independent reflections for which $I_0 > 3\sigma(I_0)$. Although deydration occurred at 360°C, no silver atoms or clusters have been observed. The 8–ring sites are occupied only by Cs^+ ion, and the 4–ring sites only by a single Ag^+ ion. The 6–ring sites contain Ag^+ and Cs^+ ions with Ag^+ nearly in 6–ring planes and Cs^+ well off them, one on the sodalite unit side. With regard to the 6–rings, the structure can be represented as a superposition of two types of unit cells: about 70% have $4Ag^+$ and $4Cs^+$ ions, and the remaining 30% have $3Ag^+$ and $5Cs^+$. In all unit cells, 3 Cs^+ ions lie at the centers of the 8–rings at sites of D_{4h} symmetry; these ions are approximately 0.3 Å further from their nearest framework–oxygen neighbors than the sum of the appropriate ionic radii would indicate. To minimize electrostatic repulsions, the Cs^+ ions at Cs(1) are not likely to occupy adjacent 6–rings in the large cavity; they are likely to be tetrahedrally arranged when there are 4.

Introduction

If completely Cs^+–exchanged zeolite A could be prepared, the total volume of exchangeable cations would be maximized (ignoring Fr^+). These ions would be extremely crowded on the inner surfaces of the zeolite, their arrangement might be novel, and the zeolite might have some unique physical properties. Unfortunately, only incomplete exchange of Cs^+ into Na_{12}–A (zeolite 4A),[1,2] K_{12}–A (zeolite 3A)[3], Tl_{12}–A[4], and Ca_6–A (zeolite 5A)[5] has been achieved so far.

This work was undertaken with the hope that complete exchange of Cs^+ for Ag^+ could be accomplished by using aqueous CsCN. It was hoped that the large formation constant[6] of $Ag(CN)_2^-$, $K_f \simeq 10^{21}$, would greatly promote the removal of Ag^+ from the zeolite, thereby facilitating the exchange process and allowing it to go to completion.

Even though the complete exchange of Cs^+ for Ag^+ was not achieved, other results have been learned, such as the structural basis for a lesser exchange limit and the relative preference of Cs^+ and Ag^+ for the coordination sites available within the zeolite. In future experiments, treatment with H_2 might lead to cluster formation, and the Cs^+ ions, by blocking 8–rings, might prevent these clusters from migrating out of the structure.

Experimental

Crystals of zeolite 4A were prepared by a modification of Charnell's method,[7] including crystallization using seed crystals from a first synthesis. A single crystal 0.08 mm on an edge was lodged in a fine glass capillary. $AgNO_3$ (0.05F) was allowed to flow past the crystal at about 1 cm/sec for two days; since the exchange of Ag^+ for Na^+ has been shown to be facile and complete after mild treatment, complete exchange was assured in this case.[8,9,10] This clear colorless crystal was further ion–exchanged by the flow method with 0.05M Cs^+ solution, a mixture of CsCN and CsOH with pH =11.4. It was then rinsed lightly with 0.05M CsOH solution, and dehydrated for 1 day at 360°C and 2×10^{-6} Torr. While still under vacuum, the crystal was allowed to cool quickly to room temperature and was sealed in its capillary by torch. Microscopic examination showed it to be brownish–yellow in color. Subsequent diffraction experiments were performed at 24 (1) °C.

The cubic space group *Pm3m* (no systematic absences) was used instead of *Fm3c* for reasons described previously.[11,12] A Syntex 4–circle computer–controlled diffractometer with a graphite monochromator and a pulse–height analyzer was used throughout for preliminary experiments and