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Studies on Aqueous Solutions of Guanidinium Salts. VIII. Free Energy of Mixing of Guanidinium Bromide and Tetrabutylammonium Bromide in Aqueous Solution at 25 °C

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Osmotic and activity coefficients have been determined by the isopiestic comparison method on the water–guanidinium bromide–tetrabutylammonium bromide system at 25 °C. The values of the excess free energy change of mixing and the interaction parameter g_0 on Friedman's formalism were large and negative in magnitude. These results have been discussed in terms of the mixed ion pairing and structural change of water.

Guanidinium salts and their related compounds are well known as protein denaturants, but the mechanism of the denaturation remains ambiguous. Two types of mechanism have so far been postulated, one is the direct interaction between the acid amide groups of proteins and denaturants leading to the destruction of the hydrogen bond between the acid amide groups and the other is the indirect interaction between proteins and denaturants through the change of water structure which stabilizes the natural conformation of protein in the aqueous solution. Robinson and Jencks[1] investigated the former mechanism by examining the effect of several perturbants on the activity coefficient of acetyltetraglycine ethyl ester. By measuring the solubility they concluded that the non-hydrophobic interaction made a major contribution to the effectiveness of perturbants in protein denaturation in aqueous solution. Kauzmann[2] and Tanford[3] suggested that the hydrophobic bond played an important role in the stability of tertiary or higher structures of proteins. In the aqueous ternary systems containing urea and hydrocarbons, urea increased the solubility of the latter.[4] Similarly the decrease in the activity coefficient of tetrabutylammonium bromide (Bu_4NBr) and a positive enthalpy of transfer were obtained for the water–urea–tetraalkylammonium salt system.[5,6] Potassium bromide, on the other hand, increased the activity coefficient of tetrapropylammonium bromide in the aqueous ternary system.[7] These results were discussed in terms of the changes of the hydrophobic interactions by the structure breaking of potassium bromide and urea.[5–7] Based on the similartities of molecular shape, size and functional groups between urea and the guanidinium ion (Gu^+), the authors postulated[8] that the mechanism of the structure breaking by the guanidinium ion was similar to that by urea rather than by large alkali metal ions such as potassium and caesium ions. The differences would be more pronounced in aqueous solutions containing structure making solutes such as tetraalkylammonium salts than in pure water. The excess thermodynamic function of mixing in aqueous electrolyte solutions has been studied mainly on inorganic salt mixtures, several cases containing tetraalkylammonium salt as a component. The free energy change of mixing of Bu_4NBr and guanidinium bromide (GuBr) has been studied by the isopiestic comparison method and the results discussed in terms of the interionic interaction and the hydrophobic hydration.

Experimental

Materials. Guanidinium bromide was obtained by concentrating the aqueous solution of guanidine neutralized with hydrobromic acid. The crystal obtained was recrystallized twice or more from acetone and dried *in vacuo* before use. Tetrabutylammonium bromide was purchased from Wako Junyaku Co., Ltd. and recrystallized twice or more from the mixed solvent (ethyl acetate: diethyl ether=3: 1).

Method. Measurements of osmotic coefficients were carried out by the isopiestic comparison method at 25±0.02 °C using the same apparatus as reported previously.[9] In order to calculate the molality of each ternary solution, buoyancy corrections were made adopting the densities of the solid as 1.894 for GuBr, 1.152 for Bu_4NBr, and unity for the aqueous solutions. Both GuBr and Bu_4NBr were used as reference solutes. The experimental determination of the isopiestic concentration were precise to within 0.5%.

Theory

Activity Coefficient. Mckay and Perring's method[10] was used to evaluate the activity coefficients of each component in the ternary solution which was prepared by mixing two kinds of 1: 1 electrolyte solutions. Under the conditions of equal vapour pressure among the three solutions, *i.e.* of GuBr (solute B), Bu_4NBr (solute C) and a mixture of both of them, the relation of Eq. 1 holds.

$$\nu_B M_B \phi_B = \nu_C M_C \phi_C = \nu m \phi, \tag{1}$$

where ν_B and ν_C are the number of moles of ions formed from 1 mol of solute B and C, M_B and M_C are the molality of solute B and C in the binary solutions which have the corresponding osmotic coefficients ϕ_B and ϕ_C, respectively. ν is the number of ions formed from 1 mol of pseudo-binary salt $(1-x)Gu^+xBu_4N^+Br^-$ and m is the total molality of the ternary solution which has the corresponding osmotic coefficient ϕ. x is the ionic mole fraction of electrolyte C in the mixture defined as

$$x = m_C/m = I_C/I, \tag{2}$$

where I_C and I are the ionic strengths of electrolyte C and the total one of the mixed electrolyte, respectively. The activity coefficient of solute B (γ_B) in the ternary solution may be obtained from the following equations:

$$\ln \gamma_B = \ln \Gamma_B + \ln R_B + \int_0^{M_B\phi_B} f(m, M_B, x)\,\mathrm{d}(M_B\phi_B) \tag{3}$$

and

$$f(m, M_B, x) = \left(\frac{\partial m}{\partial \ln x}\right)\Big/ m^2 + 1/m - 1/M_B, \tag{4}$$

where Γ_B is the activity coefficient of solute B in the binary solution in equilibrium with the ternary solution, R_B is the isopiestic ratio (M_B/m). Approximating R_B to[10])

$$R_B = 1 - a_B x - b_B x^2, \tag{5}$$

Eq. 3 reduces to

$$\ln \gamma_B = \ln \Gamma_B + \ln R_B + x^2 \int_0^{M_B\phi_B} \frac{b_B}{M_B} \mathrm{d}(M_B\phi_B). \tag{6}$$

The activity coefficient of solute C can also be obtained from the same procedure.

Free Energy of Transfer ΔG^{tr} at Constant Mole Fraction (N). Using the activity coefficient of each solute in a ternary solution calculated by the above method, the free energy of transfer of one component from the binary to the ternary solution at constant mole fraction (N) can be obtained[11]) as follows. In the case of solute C being transferred from water to a solution containing solute B, the free energy of transfer is defined as

$$\Delta G_C{}^{tr} = \nu_C RT \ln (f_C{}^*/f_C{}^0), \tag{7}$$

where $f_C{}^*$ and $f_C{}^0$ are the activity coefficients of solute C in mole fraction scale in the ternary and the binary solutions, respectively. They are defined by

$$f_C{}^0 = \gamma_C{}^0(1+0.001 M_A \nu_C m_C{}^0), \tag{8}$$

$$f_C{}^* = \gamma_C(1+0.001(\nu_C m_C{}' + \nu_B m_B)), \tag{9}$$

and

$$m_C{}' = (1+0.001 M_A \nu_B m_B) m_C{}^0, \tag{10}$$

where $m_C{}^0$ and $\gamma_C{}^0$ are the molality and the molal activity coefficient of solute C in the binary solution, while $m_C{}'$ and γ_C are the corresponding quantities in the ternary solution, having the same mole fraction (N_C) as the binary solution. M_A is the molecular weight of water. Free energy of transfer of solute B was also obtained from the same method.

Excess Free Energy Change on Mixing Solution at Constant Ionic Strength $\Delta_m G^{ex}$. $\Delta_m G^{ex}$ is defined by[12])

$$\Delta_m G^{ex}(x, I) = G^{ex}(x, I) - xG^{ex}(1, I) - (1-x)G^{ex}(0, I), \tag{11}$$

where $G^{ex}(1, I)$ and $G^{ex}(0, I)$ are the excess free energies of binary solutions of solute C and B, respectively. $G^{ex}(x, I)$ is the corresponding quantity in the ternary solution of which the total ionic strength equals I and the fraction of ionic strength is x. The excess free energy of pseudo-binary salt solutions is defined by

$$G^{ex}(x, I) = \nu RTI(\ln \gamma_\pm + (1-\phi)), \tag{12}$$

where $\gamma_\pm$ and ϕ are the mean activity coefficient and osmotic coefficient of the solute, respectively, R being the gas constant and T the absolute temperature. By applying the Gibbs-Duhem relation to Eq. 12, one obtains

$$G^{ex}(x, I) = -2\nu IRT \int_0^{\sqrt{I}} \frac{1-\phi}{\sqrt{I}} \mathrm{d}\sqrt{I}. \tag{13}$$

The integration of Eq. 13 was carried out by computer program assuming Relation 14 between ϕ and I at the same fraction x.

$$\phi = 1 - \sum_{i=1}^{5} q_i I^{i/2} \quad (q_1 = 0.3902). \tag{14}$$

Theoretically, $\Delta_m G^{ex}(x, I)$ would be expressed as a power series of the ionic strengths of each component in the mixed solution and those coefficients of the power series are related to the magnitudes of various interactions of ions. Friedman's extention based on Mayer's ionic cluster expansion theory has been adopted which yields the following expression:

$$\Delta_m G^{ex}(x, I) = I^2 RTx(1-x)(g_0 + g_1(1-2x) + \cdots), \tag{15}$$

where g_i is the interaction parameter. The first two interaction parameters of Eq. 15 were determined graphically by plotting $\Delta_m G^{ex}(x, I)/I^2 RTx(1-x)$ against x.

Results

Isopiestic Solutions. The isopiestic and related data are shown in Table 1. The second column gives the molalities of the reference GuBr solutions (M_B) having the osmotic coefficients ϕ_B. The next two columns show the molalities of GuBr (m_B) and those of Bu$_4$NBr (m_C), respectively, in the ternary solutions being isopiestic with the reference solution. The fifth shows the ionic mole fraction of solute C (x), the sixth

Table 1. Isopiestic data

Set	M_B	m_B	m_C	x	R_B
1.	0.12221	0.12221	0.0	0.0	1.0
		0.10464	0.01867	0.15141	0.99106
		0.08355	0.04107	0.32955	0.98076
		0.06425	0.06152	0.48914	0.97170
		0.04203	0.08507	0.66930	0.96167
		0.02060	0.10772	0.83944	0.95239
		0.0	0.12949	1.0	0.94380
2.	0.26367	0.26367	0.0	0.0	1.0
		0.23063	0.04062	0.14976	0.98263
		0.19278	0.08249	0.29966	0.96550
		0.17921	0.09930	0.35654	0.95906
		0.11978	0.16115	0.57367	0.93484
		0.08428	0.20066	0.70423	0.92054
		0.04607	0.25108	0.84496	0.90535
		0.0	0.29738	1.0	0.88889
3.	0.31266	0.31266	0.0	0.0	1.0
		0.28110	0.03505	0.11087	0.98894
		0.23878	0.08203	0.25569	0.97459
		0.19178	0.13415	0.41160	0.95927
		0.16472	0.16414	0.49912	0.95074
		0.07706	0.26115	0.77214	0.92444
		0.05007	0.29099	0.85319	0.91673
		0.0	0.34629	1.0	0.90289
4.	0.39966	0.39966	0.0	0.0	1.0
		0.35325	0.05422	0.13307	0.98083
		0.30481	0.11040	0.26589	0.96254
		0.23660	0.18833	0.44321	0.94053
		0.17369	0.25978	0.59931	0.92200
		0.11716	0.32431	0.73461	0.90528
		0.07196	0.37236	0.83804	0.89947
		0.0	0.44790	1.0	0.89228

TABLE 1. (Continued)

Set	M_B	m_B	m_C	x	R_B	Set	M_B	m_B	m_C	x	R_B
5.	0.53096	0.53096	0.0	0.0	1.0	12.	1.67762	1.67762	0.0	0.0	1.0
		0.44768	0.10839	0.19492	0.95484			1.57633	0.25937	0.14129	0.91389
		0.37483	0.19676	0.34424	0.92892			1.44222	0.56080	0.27998	0.83755
		0.92851	0.29312	0.49545	0.89744			1.22701	0.99595	0.44803	0.75468
		0.22420	0.37511	0.62591	0.88595			0.94534	1.41250	0.59906	0.71151
		0.15374	0.45871	0.74898	0.86694			0.57339	1.73649	0.75177	0.72628
		0.06859	0.54761	0.88868	0.86166			0.23091	1.93762	0.89352	0.77362
		0.0	0.61004	1.0	0.87030			0.0	2.03654	1.0	0.82376
6.	0.53388	0.53388	0.0	0.0	1.0	13.	1.80300	1.80300	0.0	0.0	1.0
		0.47321	0.07729	0.14040	0.96982			1.70207	0.28006	0.14129	0.90963
		0.40394	0.16405	0.28883	0.93995			1.57316	0.61171	0.27998	0.82522
		0.33408	0.25099	0.42899	0.91250			1.35551	1.10026	0.44803	0.73419
		0.26119	0.33923	0.56499	0.88917			1.04272	1.55799	0.59906	0.69327
		0.17900	0.43384	0.70792	0.87116			0.63404	1.92017	0.75177	0.70589
		0.09331	0.52753	0.84971	0.85994			0.25284	2.12126	0.89352	0.75932
		0.0	0.62391	1.0	0.85571			0.0	2.21554	1.0	0.81380
7.	0.58144	0.58144	0.0	0.0	1.0	14.	1.87978	1.87978	0.0	0.0	1.0
		0.48203	0.08059	0.14324	0.96763			1.75358	0.33271	0.15947	0.90101
		0.43461	0.18851	0.30253	0.93312			1.63252	0.66385	0.28909	0.81859
		0.36542	0.27270	0.42735	0.91119			1.42272	1.16103	0.44936	0.72754
		0.27883	0.37751	0.57515	0.88588			1.12686	1.64062	0.59282	0.67923
		0.18736	0.48208	0.72012	0.86855			0.69197	2.07502	0.74992	0.67936
		0.08706	0.59004	0.87142	0.85872			0.25058	2.34963	0.90363	0.72293
		0.0	0.67562	1.0	0.86060			0.0	2.44853	1.0	0.76772
8.	0.71676	0.71676	0.0	0.0	1.0	15.	2.39195	2.39195	0.0	0.0	1.0
		0.64232	0.10545	0.14102	0.95854			2.27552	0.49227	0.17786	0.86420
		0.56157	0.21199	0.27404	0.92658			2.16287	1.16538	0.35018	0.71868
		0.46199	0.34391	0.42674	0.88940			2.07564	1.93970	0.48307	0.59570
		0.36959	0.46041	0.55471	0.86348			1.65860	2.39766	0.59110	0.58969
		0.26635	0.57942	0.68508	0.84746			1.11530	2.92231	0.72377	0.59242
		0.11646	0.57347	0.86362	0.83937			0.57681	3.21014	0.84768	0.63163
		0.0	0.84834	1.0	0.84490			0.0	3.33282	1.0	0.71770
9.	0.87984	0.87984	0.0	0.0	1.0	16.	2.41652	2.41652	0.0	0.0	1.0
		0.80209	0.10375	0.11453	0.97130			2.30000	0.49756	0.17785	0.86363
		0.71083	0.24181	0.25383	0.92358			2.18895	1.17943	0.35015	0.71728
		0.61126	0.37979	0.38322	0.88779			2.05673	1.92202	0.48307	0.60724
		0.51319	0.50646	0.49670	0.86288			1.68454	2.43516	0.59110	0.58647
		0.25506	0.77737	0.75295	0.85220			1.13067	2.96258	0.72377	0.59025
		0.14756	0.87550	0.85576	0.86000			0.58417	3.25110	0.84768	0.62996
		0.0	1.00303	1.0	0.87718			0.0	3.37008	1.0	0.71674
10.	0.86845	0.86845	0.0	0.0	1.0	17.	2.78046	2.78046	0.0	0.0	1.0
		0.78189	0.12837	0.14102	0.95407			2.74880	0.44417	0.13911	0.87081
		0.68938	0.26023	0.27404	0.91453			2.74060	1.06264	0.27940	0.73108
		0.57048	0.42467	0.42674	0.87268			2.67769	1.97325	0.42427	0.59783
		0.45760	0.57005	0.55471	0.84509			2.37537	2.91612	0.55110	0.52546
		0.32938	0.71653	0.68508	0.83033			1.56784	3.61773	0.69765	0.53619
		0.14289	0.90486	0.86362	0.82887			0.67519	3.88295	0.85187	0.61000
		0.0	1.03178	1.0	0.84170			0.0	3.78731	1.0	0.73415
11.	1.27620	1.27620	0.0	0.0	1.0	18.	2.91109	2.91109	0.0	0.0	1.0
		1.13238	0.25725	0.18512	0.91838			2.88161	0.46563	0.13911	0.86970
		0.98478	0.52191	0.44639	0.84702			2.90398	1.12599	0.27940	0.72236
		0.80164	0.79482	0.49786	0.79940			2.88040	2.12264	0.42427	0.58187
		0.61840	1.02140	0.62288	0.77828			2.55490	3.13652	0.55110	0.51149
		0.44449	1.20608	0.73071	0.77319			1.67344	3.86139	0.69765	0.52596
		0.24695	1.37809	0.84804	0.78534			0.72096	4.14620	0.85187	0.59811
		0.0	1.55424	1.0	0.82111			0.0	3.98861	1.0	0.72985

Table 2. Osmotic coefficients of pseudo-binary salt with various ionic mole fraction x

m	$x=0.1$	$x=0.2$	$x=0.3$	$x=0.4$	$x=0.5$	$x=0.6$	$x=0.7$	$x=0.8$	$x=0.9$
0.1	0.9064	0.9022	0.8980	0.8941	0.8901	0.8860	0.8819	0.8779	0.8738
0.2	0.8783	0.8713	0.8644	0.8576	0.8511	0.8446	0.8383	0.8321	0.8261
0.3	0.8588	0.8494	0.8402	0.8312	0.8228	0.8147	0.8071	0.7998	0.7933
0.4	0.8434	0.8317	0.8204	0.8095	0.7997	0.7904	0.7822	0.7746	0.7683
0.5	0.8302	0.8163	0.8031	0.7907	0.7796	0.7696	0.7611	0.7538	0.4784
0.6	0.8186	0.8024	0.7874	0.7736	0.7616	0.7511	0.7425	0.7359	0.7319
0.7	0.8080	0.7897	0.7729	0.7579	0.7450	0.7342	0.7259	0.7203	0.7179
0.8	0.7983	0.7779	0.7593	0.7432	0.7295	0.7186	0.7109	0.7062	0.7057
0.9	0.7891	0.7665	0.7464	0.7992	0.7149	0.7039	0.6964	0.6934	0.6948
1.0	0.7804	0.7559	0.7342	0.7160	0.7011	0.6901	0.6830	0.6816	0.6849
1.2	0.7640	0.7358	0.7112	0.6911	0.6751	0.6643	0.6583	0.6599	0.6670
1.4	0.7487	0.7173	0.6900	0.6681	0.6511	0.6405	0.6356	0.6402	0.6505
1.6	0.7341	0.7001	0.6703	0.6467	0.6287	0.6183	0.6144	0.6216	0.6346
1.8	0.7201	0.6839	0.6521	0.6267	0.6077	0.5975	0.5945	0.6039	0.6187
2.0	0.7068	0.6687	0.6351	0.6079	0.5882	0.5780	0.5757	0.5867	0.6027
2.5	0.6765	0.6345	0.5975	0.5662	0.5447	0.5341	0.5328	0.5455	0.5615
3.0	0.6524	0.6044	0.5652	0.5307	0.5081	0.4966	0.4954	0.5067	0.5207
3.5	0.6380	0.5770	0.5357	0.4999	0.4773	0.4646	0.4630	0.4715	0.4849
4.0	0.6377	0.5508	0.5060	0.4719	0.4505	0.4371	0.4353	0.4416	0.4606

the isopiestic ratio (R_B).

Activity Coefficients. The activity coefficients of guanidinium bromide (γ_B) and tetrabutylammonium bromide (γ_C) for various ionic mole fractions obtained from Mckay and Perring's method are shown in Figs. 1 and 2, respectively. Each activity coefficient decreased as the total molality increased. In the system of the common ion mixing, the log γ curves for each electrolyte in aqueous ternary solutions with constant ionic mole fraction plotted against the total molality are usually located between those curves for the two binary systems. Put another way, the higher log γ values of the two electrolytes decreases on moving from the binary system to the ternary one, and *vice versa*. As shown in Fig. 1, the log γ values of guanidinium bromide in the H$_2$O–GuBr–Bu$_4$NBr system obeyed this rule in the concentration range studied, since the log γ values of GuBr (log $\gamma_B{}^0$) were higher than those of Bu$_4$NBr (log $\gamma_C{}^0$) in each binary solution at the same molalities. As seen in Fig. 2, the activity coefficients of Bu$_4$NBr (log γ_C) in this ternary system were higher than those in the binary solution (log $\gamma_C{}^0$) below 1 molal, while the log γ_C values were lower than log $\gamma_C{}^0$ above 1 molal. Therefore the two curves cross each other around 1 molal. In order to express more clearly the influence of one electrolyte on the activity coefficient of the other in the ternary system, extended Harned's equation have been proposed as follows:[13,14)]

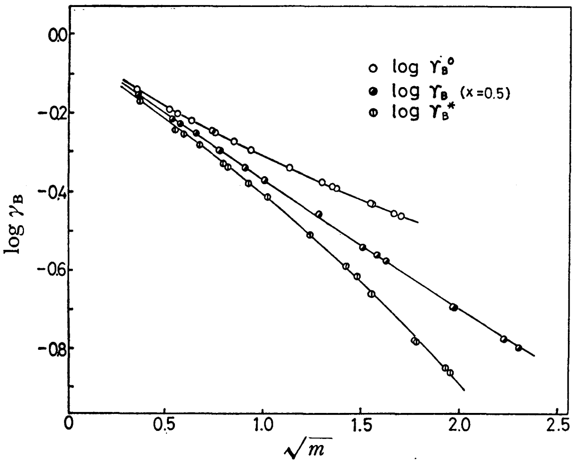

Fig. 1. Activity coefficient of GuBr (solute B) γ_B, plotted against $\sqrt{m}$. $\gamma_B{}^0$ is the activity coefficient in binary solution of solute B. $\gamma_B{}^*$ is the activity coefficient of solute B in the solution containing only solute C (trace activity coefficient of B).

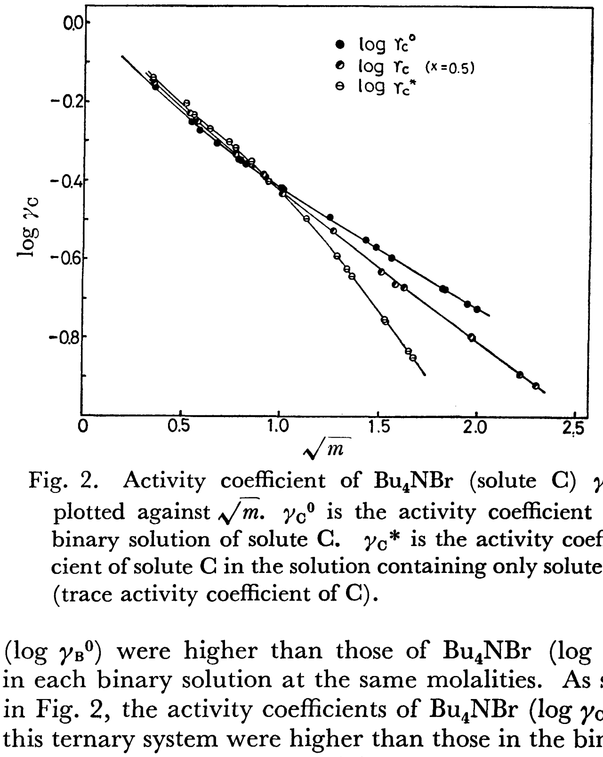

Fig. 2. Activity coefficient of Bu$_4$NBr (solute C) γ_C, plotted against $\sqrt{m}$. $\gamma_C{}^0$ is the activity coefficient in binary solution of solute C. $\gamma_C{}^*$ is the activity coefficient of solute C in the solution containing only solute B (trace activity coefficient of C).

$$\begin{aligned}\log\gamma_B &= \log\gamma_B{}^0 - \alpha_B m_C - \beta_B m_C{}^2\\ &= \log\gamma_B{}^0 - \alpha_B m x - \beta_B m^2 x^2 \qquad (16)\end{aligned}$$

and

$$\begin{aligned}\log\gamma_C &= \log\gamma_C{}^0 - \alpha_C m_B - \beta_C m_B{}^2\\ &= \log\gamma_C{}^0 - \alpha_C m(1-x) - \beta_C m^2(1-x)^2, \qquad (17)\end{aligned}$$

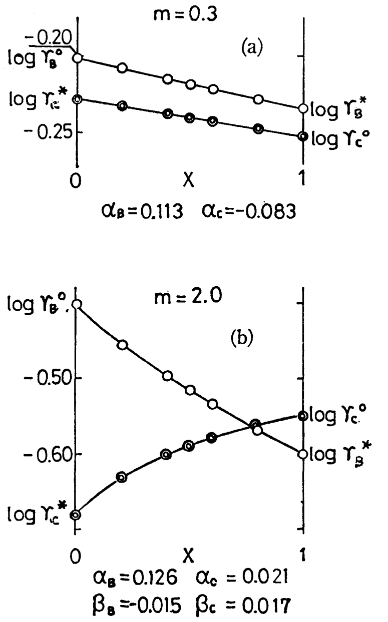

Fig. 3. (a) The variation of two activity coefficients against x at the total molality of 0.3. (b) The variation of two activity coefficients against x at the total molality of 2.0.

where α and β are the empirical constants which represent the type and magnitude of interionic interactions. In Figs. 3-a and 3-b, the relation between the activity coefficient of each salt and the mole fraction of Bu_4NBr (x) are shown at total molality 0.3m and 2.0m, respectively. In Fig. 3-a, log γ_B decreases almost linearly with the increase of x, log γ_C increases from log $\gamma_C{}^0$ to log $\gamma_C{}^*$ (trace activity coefficient of Bu_4NBr) linearly as x decreases from 1 to 0. The values of α_B and α_C were 0.113 and —0.083, respectively, and the values of β were nearly zero. As seen in Fig. 3-b, however, an abnormal change appeared when the total molality was at 2.0m. The values of log γ_B decreased with the increase of value of x, while log γ_C decreased with the decrease of x. Therefore, the two curves were non-linear and the values of α_B and α_C were 0.126 and 0.021, respectively, while β_B and β_C were —0.015 and 0.017, respectively. Curves of this type which cross have so far been rarely reported in aqueous ternary solutions containing two kinds of inorganic electrolytes.

Free Energy of Transfer ΔG^{tr}. It is difficult to distinguish whether the change of the activity coefficient are based on salting-out, salting-in or "mutual" effect by plotting the activity coefficients at constant x against total molality. In the case of ΔG^{tr}, it is distinguishable because the free energy of transfer can be calculated from Eqs. 7—10, converting the activity coefficients to those in the mole fraction scale. They are shown in Tables 3-a and 3-b. Negative values of ΔG^{tr} were obtained for each electrolyte and the absolute value of ΔG^{tr} for each electrolyte increased with the molality of the other.

TABLE 3-a. FREE ENERGY OF TRANSFER OF TETRABUTYLAMMONIUM BROMIDE FROM WATER TO GUANIDINIUM BROMIDE SOLUTION AT CONSTANT MOLE FRACTION N_C

m_C	N_C	m_B			
		0.5	1.0	2.0	3.0
0.0	0.0000	−776	−1116	−1994	−2304
0.5	0.0089	−278	−475	−932	−1357
1.0	0.0174	−181	−386	−768	−1090

TABLE 3-b. FREE ENERGY OF TRANSFER OF GUANIDINIUM BROMIDE FROM WATER TO TETRABUTYLAMMONIUM BROMIDE SOLUTION AT CONSTANT MOLE FRACTION N_B

m_B	N_B	m_C			
		0.5	1.0	2.0	3.0
0.0	0.0000	−790	−1076	−1530	−1924
0.5	0.0089	−200	−548	−956	−1302
1.0	0.0174	−141	−508	−871	−1168

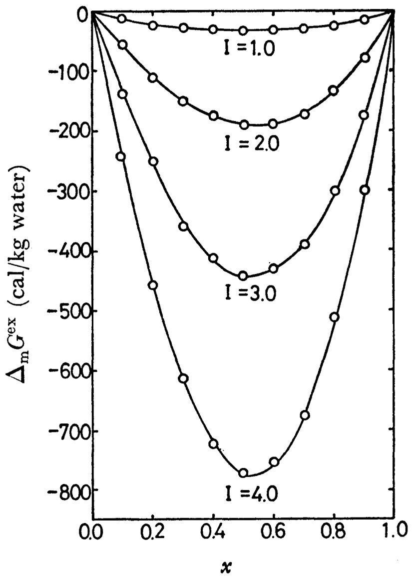

Fig. 4. Excess free energy change of mixing $\Delta_m G^{ex}$ against x at the constant total ionic strength I.

TABLE 4. INTERACTION PARAMETERS, g_0 AND g_1

I	g_0(mol^{-1})	g_1 (mol^{-1})
0.5	−0.1362	0.0148
1.0	−0.2382	0.0298
1.5	−0.2965	0.0530
2.0	−0.3228	0.0581
2.5	−0.3298	0.0539
3.0	−0.3273	0.0466
3.5	−0.3221	0.0386
4.0	−0.3219	0.0386

Excess Free Energy Change of Mixing $\Delta_m G^{ex}$. The osmotic coefficients of pseudo-binary salts (ϕ) for various ionic mole fraction x are shown in Table 2. These values were read from the ϕ-I curves obtained by a least squares fit to Eq. 14. $\Delta_m G^{ex}$ at constant ionic strength was obtained from Eqs. 13 and 11 as shown in Fig. 4. The curves are nearly parabolic but the minimum point is slightly displaced towards the right from the

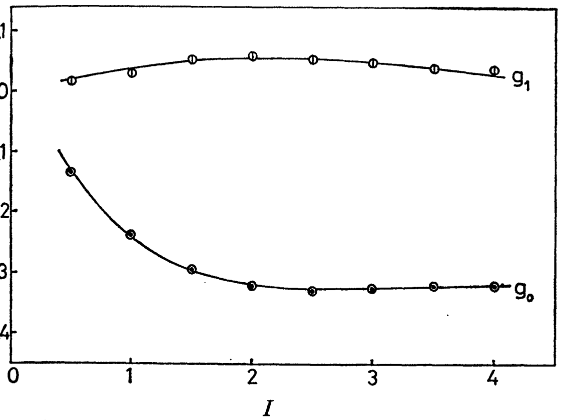

Fig. 5. Interaction parameters g_0 and g_1 plotted against I.

vertical line of $x=0.5$. The value of $\Delta_m G^{ex}$ at the minimum decreases as the total ionic strength increases. The interaction parameters g_0 and g_1 obtained from Eq. 15 are shown in Fig. 5 and Table 4. The negative values of g_1 slightly increased up to about $I=2.0$ and decreased with the increase of I.

Discussion

In most aqueous ternary systems containing two kinds of inorganic electrolytes with a common anion, the relation between log γ and the concentration of each electrolyte obeys "Harned's rule" for a wide range of concentration.[14] This means that the values the interaction parameter for a mixed cation pair corresponds almost to the arithmetic mean value of those for like cation pairs.[15] As shown in Fig. 3-a, the system of H_2O–GuBr–Bu_4NBr showed a similar behavior at low concentration to the aqueous ternary systems with two kinds of inorganic electrolytes, although the slopes of the log γ *vs.* x curves were considerably larger. However, as seen in Fig. 3-b, when the total molality increased, the log γ *vs.* x curves were quite different from those of Fig. 3-a. This implies that Harned's rule does not hold at high concentration, that is, the attractive interaction between Bu_4N^+ and Gu^+ increases and dominates the other pair interactions. This salting-in effect is expressed in terms of the free energy of transfer ΔG^{tr} similar to that of the H_2O–urea–Bu_4NBr system. The values of ΔG^{tr} for Bu_4NBr in the H_2O–GuBr–Bu_4NBr system are almost twice as large as those in the H_2O–urea–Bu_4NBr system.[5] This result is closely related to the effective concentration of these solutes in the denaturation of proteins in aqueous solutions. As seen in Fig. 4, the values of $\Delta_m G^{ex}$ are all negative and depend parabolically on x at all ionic strengths, suggesting that the g_0 terms are more important than the g_1 terms in the concentration region studied.[7] However the skewness of the curves at high ionic strength shows that the g_1 terms cannot be ignored. As shown in Fig. 5 and Table 4, the positive g_1 values increased as the concentration increased up to around $2.0m$ and decreased above this concentration. However the magnitudes of g_0 are 6 or 10 times larger than those of g_1. In the symmetrical mixture of electrolyte, g_0 and g_1 are expressed as[16]

$$g_0 = (g^{B^+C^+} - g^{B^+B^+} - g^{C^+C^+}) + I(g^{B^+C^+Br^-} - g^{B^+B^+Br^-} - g^{C^+C^+Br^-}) + \text{triplet type of same cations} \quad (18)$$

and

$$g_1 = I(g^{B^+C^+C^+} - g^{B^+B^+C^+} + g^{B^+B^+B^+} - g^{C^+C^+C^+}), \quad (19)$$

where B^+ and C^+ are Gu^+ and Bu_4N^+, respectively, and g^{ij} is the interaction parameter of free energy of ions i and j, g^{ijk} is the same quantity of three ions i, j, and k. Though it will be of great interest to find the values of g^{ij} and g^{ijk}, it is quite impossible using this experimental approach. The g_0 coefficients listed in Table 4 are related to the coefficient of Harned's equation[12] as

$$g_0 = -2.303((\alpha_B+\alpha_C) + I(\beta_B+\beta_C)) + \cdots. \quad (20)$$

The pairwise interaction parameter in Eq. 18, $(g^{B^+C^+} - g^{B^+B^+} - g^{C^+C^+})$ corresponds to $-2.303\ (\alpha_B+\alpha_C)$. The values of this ion pair term at $0.3m$ and $2.0m$ are -0.069 and -0.339, respectively. The sign and magnitude of the values at $2.0m$ are almost the same as those of g_0 in Table 4 suggesting that the pairwise interaction is quite important at this concentration. The negative sign of the pairwise interaction term implies that the mixed cation pair Gu^+–Bu_4N^+ is more favored over the like ion pairs Gu^+–Gu^+ and Bu_4N^+–Bu_4N^+. In a previous paper,[17] it was reported that guanidinium bromide formed a crystalline complex with tetrabutylammonium bromide at high concentrations in aqueous solutions. From this fact and the large negative values of the pairwise interaction term in Eq. 18 at moderate concentrations, it seems plausible that the formation of mixed cation pair, Gu^+–Bu_4N^+ makes an important contribution to the mutual salting-in. However, Friedman's treatment is not sufficiently rigorous in which water is regarded as a continuum solvent with the dielectric constant of 80. Therefore the interionic interaction through the change of water structure caused by the addition of ions has to be considered. This effect may work as an attractive or repulsive force between ions. Previously,[9] the guanidinium ion was reported to be a structure breaker ion, while Bu_4N^+ was regarded as a hydrophobic structure maker which formed the clathrate hydrate in aqueous solution. As pointed out in a previous paper,[8] the interaction between Gu^+ and Bu_4N^+ decreases the water structure around Bu_4N^+. This effect also makes a negative contribution to g_0 values even if these two kinds of cations do not form a mixed ion pair.

It is interesting to compare $\Delta_m G^{ex}$ and ΔG^{tr} of this system and those of the H_2O–KBr–Pr_4NBr[7] and H_2O–urea–Bu_4NBr[5] systems. In the H_2O–KBr–Pr_4NBr system, $\Delta_m G^{ex}$ *vs.* x curves are usually parabolic as in the case of this system, but the sign of $\Delta_m G^{ex}$ is opposite. Wen[6] and Wood[18] concluded from the measurements of free energy and heats of mixing that Pr_4N^+–Pr_4N^+ was favored over the mixed ion pair in that system. Both the potassium[20] and guanidinium ions are classified as structure breakers but the mechanism of the breaking of the water structure should be quite different from each other,[7,8] since the effects of those ions toward hydrophobic hydration are quite different. On the other hand, ΔG^{tr} of Bu_4NBr from water to the aqueous solutions of urea and GuBr are both negative and the magnitudes of ΔG^{tr} are comparable to each other.

These results suggest that the shape, size, and functional groups play important roles in the effect of organic solutions on hydrophobic hydration at high concentration. The next stage, in progress now, is to measure the heat of mixing of these salts in aqueous solution.

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