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Free Energy, Enthalpy, and Entropy Changes of Mixing of Aqueous Solutions of D-Glucose and Tetraalkylammonium Bromide at 25 °C

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Changes of free energy and enthalpy of mixing of aqueous solutions of D-glucose and tetraalkylammonium bromide were measured at 25 °C by isopiestic method and calorimetry, and excess thermodynamic quantities and transfer functions were calculated. All transfer functions were positive and mutual salting-out was observed. The positive value of free energy of transfer of tetrabutylammoniun bromide from water to aqueous D-glucose solution comes from the predominance of enthalpic term over entropic term. These results are interpreted in terms of the structural incompatibility of hydration cospheres around these two kinds of solutes.

The tetraalkylammonium salt (TAAB) is known to enhance the structure of water by formation of a cage-like structure around itself. Judging from the results of x-ray analysis of the tetrabutylammonium fluoride,[1)] the hydrogen bond network of clathrate compound is different from that of tridymite structure of ice, though the hydrogen bond length and the bond angle are similar.

Various monosaccharides, such as D-glucose, also promote the water structure by directly forming hydrogen bonds with water molecules. Kabayama and Patterson[2)] postulated that the spacing of the equatorial oxygen atoms of the hexopyranose of the chair conformation nearly fits the spacing of oxygen atoms in the tridymite-like structure of water. In a previous paper,[3)] we reported the excess thermodynamic quantities of aqueous monosaccharide solutions, and concluded D-glucose to be a structure maker from the negative value of excess partial molar entropy of water. Therefore, the water structure around D-glucose and that around the tetraalkylammonium bromide must be different from each other.

On the other hand, various saccharides and polyalcohols are reported to be an anti-denaturating agents of proteins in aqueous solutions,[4)] and the mechanism is considered to be related to the strengthening of hydrophobic interaction in protein molecule by the presence of these compounds. Therefore, the study on the structural interaction of these two kinds of solutes, one is hydrophobic solute and the other hydrophilic, in aqueous solutions seems to be important as a model system of such a protein denaturation in aqueous solutions.

From these points of view, we measured the activity coefficients and heat of dilution on the ternary system D-glucose–tetrabutylammonium bromide (TBAB)–water at 25 °C, and discussed the interaction of these solutes through the structural change of water on the basis of the thermodynamic excess quantities and the transfer functions.

Theory

Activity Coefficient. Activity coefficients of solutes 1 (D-glucose) and 2 (TAAB) are determined from the isopiestic data by the Ellerton-Dunlop method.[5)] Assume that the activity coefficient of solute 1 (γ_1) is expressed by Eq. 1.

$$\ln \gamma_1 = \sum_{i=0}^{4}\sum_{j=0}^{4} g_{ij} m_1^i m_2^j \quad (A_{00}=0,\ i+j \leq 4), \tag{1}$$

where g_{ij}'s are the interaction parameters and m_1 and m_2 the molalities of solutes 1 and 2, respectively. In Eq. 1, the four terms $g_{10}m_1$, $g_{20}m_1^2$, $g_{30}m_1^3$, and $g_{40}m_1^4$ correspond to the contributions of activity coefficient of binary system (γ_1°). Therefore, Eq. 1 is rewritten as

$$\ln \gamma_1 = \ln \gamma_1^\circ + g_{01}m_2 + g_{11}m_1m_2 + g_{02}m_2^2 + g_{21}m_1^2m_2 + g_{12}m_1m_2^2 + g_{03}m_2^3 + g_{31}m_1^3m_2 + g_{22}m_1^2m_2^2 + g_{13}m_1m_2^3 + g_{04}m_2^4. \tag{2}$$

Here the cross differential relation holds between two solutes.

$$\left(\frac{\partial \ln \gamma_1}{\partial m_2}\right)_{m_1} = \nu \left(\frac{\partial \ln \gamma_2}{\partial m_1}\right)_{m_2}, \tag{3}$$

where ν is the number of moles of ions formed from 1 mole of solute 2 (TAAB). Introducing Eq. 2 to Eq. 3, we obtain Eq. 4 as an expression of activity coefficient for solute 2.

$$\nu \ln \gamma_2 = \nu \ln \gamma_2^\circ + g_{01}m_1 + \frac{1}{2}g_{11}m_1^2 + 2g_{02}m_1m_2 + \frac{1}{3}g_{21}m_1^3 + g_{12}m_1^2m_2 + 3g_{03}m_1m_2^2 + \frac{1}{4}g_{31}m_1^4 + \frac{2}{3}g_{22}m_1^3m_2 + \frac{3}{2}g_{13}m_1^2m_2^2 + 4g_{04}m_1m_2^3. \tag{4}$$

Combining Eqs. 2 and 4 with Gibbs-Duhem relation, experimental quantity defined by Eq. 5 is expressed by Eq. 6 using g_{ji}'s.

$$\Delta = \nu_R m_R \phi_R - m_1\phi_1^\circ - \nu m_2 \phi_2^\circ, \tag{5}$$

and

$$\Delta/m_1m_2 = g_{01} + g_{11}m_1 + 2g_{02}m_2 + g_{21}m_1^2 + \frac{3}{2}g_{12}m_1m_2 + 3g_{03}m_2^2 + g_{31}m_1^3 + \frac{4}{3}g_{22}m_1^2m_2 + 2g_{13}m_1m_2^2 + 4g_{04}m_2^3. \tag{6}$$

In these equations, ν_R is the number of moles of ions produced by the dissociation of 1 mol of reference salt, and m_R and ϕ_R are the molality and the osmotic coefficient of reference salt, respectively. ϕ_1° and ϕ_2° are osmotic coefficients of solutes 1 and 2 in binary aqueous solutions, respectively. The activity coefficients of solutes 1 and 2 can be calculated from g_{ij}'s obtained by the application of the least squares method to Eq. 6.

Heat of Dilution. Assume that the excess enthalpy of ternary system is expressed by the polynomials involving terms up to quartic.

$$H^{\mathrm{ex}} = (m_1\phi_{\mathrm{L.1}}^{\mathrm{ex,0}} + m_2\phi_{\mathrm{L.2}}^{\mathrm{ex,0}}) + h_{11}m_1m_2 + h_{21}m_1^2m_2 + h_{12}m_1m_2^2 + h_{31}m_1^3m_2 + h_{22}m_1^2m_2^2 + h_{13}m_1m_2^3, \tag{7}$$

where $\phi_{\mathrm{L.1}}^{\mathrm{ex,0}}$ and $\phi_{\mathrm{L.2}}^{\mathrm{ex,0}}$ are the apparent molar excess enthalpies in aqueous binary solutions, and h_{ij}'s are interaction parameters. M and x being the total molality and the mole fraction of solute 1, respectively, excess mean apparent molar enthalpy ($\phi_{\mathrm{L}}^{\mathrm{ex}}$) is expressed by Eq. 8.

$$\phi_{\mathrm{L}}^{\mathrm{ex}} = H^{\mathrm{ex}}/M = [x\phi_{\mathrm{L.1}}^{\mathrm{ex,0}} + (1-x)\phi_{\mathrm{L.2}}^{\mathrm{ex,0}}] + h_{11}x(1-x)M + h_{21}x^2(1-x)M^2 + h_{12}x(1-x)^2M^2 + h_{31}x^3(1-x)M^3 + h_{22}x^2(1-x)^2M^3 + h_{13}x(1-x)^3M^3. \tag{8}$$

$$(M=m_1+m_2,\ x=m_1/M)$$

Q_{D} is defined as mean molar heat evolved on dilution from M to M', then Q_{D} is expressed by

$$-Q_{\mathrm{D}}(M \rightarrow M') = \phi_{\mathrm{L}}^{\mathrm{ex}}(x, M) - \phi_{L}^{\mathrm{ex}}(x, M'). \tag{9}$$

Introducing Eq. 8 to Eq. 9, we obtain

$$\begin{aligned} &\mathrm{Q}_{\mathrm{D}}(M \rightarrow M') - x[\phi_{\mathrm{L.1}}^{\mathrm{ex,0}}(xM) - \phi_{\mathrm{L.1}}^{\mathrm{ex,0}}(xM')] \\ &- (1-x)\{\phi_{\mathrm{L.2}}^{\mathrm{ex,0}}[(1-x)M] - \phi_{\mathrm{L.2}}^{\mathrm{ex,0}}[(1-x)M']\} \\ &= h_{11}x(1-x)(M-M') + h_{21}x^2(1-x)(M^2-M'^2) \\ &+ h_{12}x(1-x)^2(M^2-M'^2) + h_{31}x^3(1-x)(M^3-M'^3) \\ &+ h_{22}x^2(1-x)^2(M^3-M'^3) + h_{13}x(1-x)^3(M^3-M'^3). \end{aligned} \tag{10}$$

The left hand terms of Eq. 10 can be experimentally measurable quantities, because the first term corresponds to the enthalpy of dilution of ternary system and the second and the third terms correspond to the enthalpy of dilution of each binary system. Therefore, Q_{D} was measured with variations of total molarities and degree of dilution, and the interaction parameters were determined by the least squares method. H^{ex} and $\phi_{\mathrm{L}}^{\mathrm{ex}}$ were calculated from these h_{ij}'s using Eqs. 7 and 8.

Excess Thermodynamic Quantities of Mixing. Excess free energy change of mixing of each component is expressed by the Eqs. 11, 12, and 13.[6,8]

$$\Delta_{\mathrm{m}}G_1^{\mathrm{ex}} = RTm_1 \ln(\gamma_1/\gamma_1^{\circ}), \tag{11}$$

$$\Delta_{\mathrm{m}}G_2^{\mathrm{ex}} = \nu RTm_2 \ln(\gamma_2/\gamma_2^{\circ}), \tag{12}$$

and

$$\Delta_{\mathrm{m}}G_{\mathrm{w}}^{\mathrm{ex}} = -RT\Delta, \tag{13}$$

where subscripts 1, 2, and w denote D-glucose, TAAB, and water, respectively. Total excess free energy change of mixing is the sum of three components.

$$\Delta_{\mathrm{m}}G^{\mathrm{ex}} = \Delta_{\mathrm{m}}G_1^{\mathrm{ex}} + \Delta_{\mathrm{m}}G_2^{\mathrm{ex}} + \Delta_{\mathrm{m}}G_{\mathrm{w}}^{\mathrm{ex}}. \tag{14}$$

Excess enthalpy change of mixing is expressed by Eq. 15·

$$\Delta_{\mathrm{m}}H^{\mathrm{ex}} = H^{\mathrm{ex}} - m_1\phi_{\mathrm{L.1}}^{\mathrm{ex}} - m_2\phi_{\mathrm{L.2}}^{\mathrm{ex}}. \tag{15}$$

Therefore, excess entropy change of mixing is obtained from $\Delta_{\mathrm{m}}G^{\mathrm{ex}}$ and $\Delta_{\mathrm{m}}H^{\mathrm{ex}}$,

$$\Delta_{\mathrm{m}}S^{\mathrm{ex}} = (\Delta_{\mathrm{m}}H^{\mathrm{ex}} - \Delta_{\mathrm{m}}G^{\mathrm{ex}})/T. \tag{16}$$

Change of the Partial Molar Thermodynamic Quantities of Transfer of the Solute from Water to Aqueous Solution; Thermodynamic Transfer Functions. Free energy change on transferring 1 mol of solute 1 from water to aqueous solution ($\Delta\bar{G}_1^{\mathrm{tr}}$) is expressed by Eq. 17.

$$\Delta\bar{G}_1^{\mathrm{tr}} = RT\ln(\gamma_1/\gamma_1^{\circ}). \tag{17}$$

Similarly in the case of solute 2 $\Delta\bar{G}_2^{\mathrm{tr}}$ is expressed by Eq. 18.

$$\Delta\bar{G}_2^{\mathrm{tr}} = \nu RT\ln(\gamma_2/\gamma_2^{\circ}). \tag{18}$$

Partial molar enthalpy change on transferring 1 mol of solute 1 or solute 2 from water to aqueous solution is expressed by Eq. 19 or Eq. 20.

$$\begin{aligned} \Delta\bar{H}_1^{\mathrm{tr}} &= \left(\frac{\partial\Delta_{\mathrm{m}}H^{\mathrm{ex}}}{\partial m_1}\right)_{m_2} \\ &= h_{11}m_2 + 2h_{21}m_1m_2 + h_{12}m_2^2 + 3h_{31}m_1^2m_2 + 2h_{22}m_1m_2^2 + h_{13}m_2^3, \end{aligned} \tag{19}$$

or

$$\begin{aligned} \Delta\bar{H}_2^{\mathrm{tr}} &= \left(\frac{\partial\Delta_{\mathrm{m}}H^{\mathrm{ex}}}{\partial m_2}\right)_{m_1} \\ &= h_{11}m_1 + h_{21}m_1^2 + 2h_{12}m_1m_2 + h_{31}m_1^3 + 2h_{22}m_1^2m_2 + 3h_{13}m_1m_2^2. \end{aligned} \tag{20}$$

Therefore, partial molar entropy change on transferring 1 mol of solute 1 or solute 2 from water to aqueous solution is written by Eq. 21.

$$\Delta\bar{S}_k^{\mathrm{tr}} = (\Delta\bar{H}_k^{\mathrm{tr}} - \Delta\bar{G}_k^{\mathrm{tr}})/T. \quad (k=1 \text{ or } 2) \tag{21}$$

Experimental

Materials. Reagent grade D-glucose obtained from Nakarai Chemical Co. Ltd., was dried *in vacuo* for several days at room temperature over P_2O_5 before use. TBAB and TMAB purchased from Nakarai Chemical Co. Ltd. were recrystallized twice from appropriate solvent described elsewhere,[7] and dried *in vacuo* for 2 d at 80 °C before use. Reagent grade sodium chloride was obtained from Matsunaga Chemical Co. Ltd., and dried *in vacuo* for a day at 100 °C. Solutions were prepared with water purified by distillations and deionization.

Methods. Osmotic coefficients were measured at 25±0.2 °C by isopiestic comparison method described elsewhere.[8] Sodium chloride and TBAB were used as reference solutes. Measurement of heat of dilution was carried out by using a flow microcalorimeter (LKB 10700-1) at 25±0.001 °C. Experimental procedure and accuracy were the same as those reported elsewhere.[9] The least squares fittings were carried out by using FACOM OSIV/F4 in Data Processing Center of Kyoto university.

Results

Activity Coefficient. Isopiestic molalities of solutes 1 (D-glucose) and 2 (TAAB) in the ternary systems and of the reference solutes are shown in Table 1 together with the experimental quantity Δ/m_1m_2 and percentage errors (Diff. %) defined by Kelly *et al.*[10] The osmotic coefficients of aqueous binary solutions were taken from the literatures given by Robinson and Stokes[11] for NaCl, Lindenbaum and Boyd[12] and Wen *et al.*[13] for TBAB, Levien[14] for TMAB, and authors[3] for D-glucose. Parameters in Eq. 6 calculated from the data in Table 1 by the least squares method were shown in Table 2. The activity coefficient *vs.* molality curves for D-glucose and TBAB in binary and ternary solutions are shown in Figs. 1 and 2, respectively. The activity coefficient of

Table 1. Isopiestic data for the ternary systems at 25 °C

m_{R}[a]	m_1	m_2	Δ/m_1m_2	Diff.%
	D-Glucose–TBAB–Water			
5.58547[b]	1.88173	2.43312	0.106_7	0.23
	2.45491	1.66757	0.143_9	0.28
	3.01205	1.09892	0.183_5	0.56
	3.51991	0.69762	0.211_7	0.83
4.83019[b]	1.01674	3.07606	0.087_3	0.79
	1.63818	2.11820	0.130_4	−0.05
	2.16277	1.46913	0.174_0	0.02
	2.67844	0.97721	0.217_0	0.28
	3.14644	0.62360	0.247_6	0.54
	3.59751	0.34642	0.261_8	0.71
3.01293[b]	0.63513	2.05193	0.152_1	0.45
	1.13429	1.44160	0.199_1	0.63
	1.45981	1.10247	0.244_0	0.39
	1.90703	0.73042	0.284_2	0.84
	2.35036	0.42425	0.324_6	0.81
	2.78284	0.18193	0.361_5	0.39
2.55046[b]	0.54959	1.77558	0.173_3	0.54
	0.99392	1.26320	0.230_6	0.44
	1.29479	0.97784	0.262_9	0.70
	1.69558	0.64943	0.310_2	0.79
	2.09777	0.37865	0.350_0	0.75
	2.49051	0.16282	0.388_6	0.34
3.19897	4.11496	1.05103	0.170_0	0.92
	4.63770	0.66049	0.194_4	0.68
	5.23109	0.30484	0.219_3	0.29
3.04387	1.22289	4.79463	0.064_4	−0.63
	2.51047	2.53846	0.111_9	0.29
	2.98874	1.86965	0.139_0	−0.30
	3.48175	1.34172	0.163_6	0.00
	3.90509	0.96251	0.190_2	−0.05
	4.34530	0.63886	0.214_8	−0.08
	4.89791	0.31015	0.240_1	−0.12
3.02745	1.17178	4.91373	0.051_7	−0.15
	2.48856	2.56977	0.104_8	0.94
	2.97920	1.88543	0.130_2	0.42
	3.48210	1.32319	0.161_6	0.23
	3.85308	0.98530	0.186_7	0.07
	4.35193	0.62052	0.211_7	0.12
	4.92406	0.28729	0.229_3	0.17
3.00226	1.18078	4.79459	0.056_1	−0.05
	2.50085	2.47096	0.109_9	0.48
	2.98549	1.81767	0.134_5	0.24
	3.38927	1.36985	0.159_2	0.19
	3.82790	0.96826	0.188_5	0.06
	4.31823	0.60771	0.216_4	−0.00
	4.79664	0.32369	0.236_7	−0.02
2.95340	1.17417	4.60363	0.064_9	−0.23
	1.88423	3.32784	0.083_4	−1.42
	2.41522	2.44214	0.115_2	−0.22
	2.88180	1.80275	0.143_4	−0.57
	3.35513	1.29293	0.172_9	−0.41
	3.77127	0.92953	0.198_7	−0.29
	4.20068	0.61759	0.223_3	−0.23
	4.73634	0.29992	0.250_3	−0.23
2.86386	1.11887	4.38683	0.071_4	−0.34
	1.80350	3.18527	0.088_1	0.66
	3.22973	1.24460	0.183_5	−0.77
	3.63781	0.89664	0.209_1	−0.52
	4.05782	0.59659	0.233_0	−0.36
	4.56492	0.28907	0.276_0	−0.63
2.69620	1.02361	4.01334	0.078_5	−0.17
	1.66112	2.93380	0.094_6	0.12
	2.57995	1.61393	0.160_1	−0.76
	3.01173	1.16060	0.198_2	−0.82
	3.40422	0.83906	0.222_0	−0.43
	3.79793	0.55838	0.249_8	−0.39
	4.29541	0.27200	0.272_1	−0.20
2.67229	0.97211	4.07643	0.068_2	0.47
	1.65960	2.86335	0.097_7	−0.02
	2.10914	2.17797	0.124_8	−0.49
	2.55073	1.61427	0.156_0	−0.42
	3.00739	1.14280	0.192_7	−0.33
	3.34902	0.85640	0.216_4	−0.16
	3.80127	0.54200	0.238_2	0.14
	4.31330	0.25165	0.247_5	0.35
2.44087	0.85889	3.48754	0.080_6	0.66
	1.35217	2.66616	0.113_5	−0.50
	1.90085	1.87813	0.152_0	−0.76
	2.30898	1.40578	0.185_9	−0.58
	2.65214	1.07192	0.217_4	−0.50
	3.02725	0.76574	0.248_9	−0.37
	3.44249	0.48446	0.276_4	−0.19
	3.88367	0.25905	0.299_9	−0.16
2.37975	0.84140	3.29891	0.096_6	0.03
	1.38237	2.44149	0.127_2	−0.77
	1.81172	1.83192	0.163_9	−1.12
	2.20690	1.38056	0.198_4	−0.96
	2.60620	1.00432	0.234_8	−0.76
	2.95772	0.72901	0.262_5	−0.52
	3.32277	0.48852	0.282_1	−0.18
	3.76170	0.23820	0.314_6	−0.25
2.20377	0.73640	2.99016	0.103_7	0.33
	1.17137	2.30968	0.134_5	−0.32
	1.67033	1.65037	0.175_6	−0.37
	2.04440	1.24470	0.213_6	−0.36
	2.36286	0.95500	0.244_6	−0.25
	2.70716	0.68477	0.277_8	−0.21
	3.09209	0.43515	0.301_4	0.04
	3.44982	0.23281	0.333_9	−0.18
2.00818	0.66368	2.57654	0.126_0	0.18
	1.10181	1.98079	0.140_5	0.84
	1.46915	1.50836	0.188_5	0.25
	1.83187	1.13442	0.228_1	0.25
	2.13293	0.87272	0.257_2	0.39
	2.44249	0.63582	0.288_0	0.38
	2.79087	0.41377	0.305_7	0.63
	3.12781	0.22434	0.329_3	0.38
1.84657	0.62926	2.18474	0.178_6	−0.92
	1.01585	1.68954	0.197_8	−0.55
	1.34154	1.32358	0.232_8	−0.53
	1.67233	1.00653	0.269_9	−0.42
	1.97911	0.75860	0.297_0	−0.06
	2.23993	0.56952	0.323_4	0.01
	2.55794	0.37676	0.333_5	0.48
	2.92561	0.17304	0.387_5	−0.11

TABLE 1. (Continued)

m_R [a)]	m_1	m_2	Δ/m_1m_2	Diff.%
1.72165	0.53468	2.07574	0.159_4	0.19
	0.90015	1.61826	0.184_4	0.58
	1.22334	1.25599	0.228_3	0.34
	1.54421	0.95628	0.263_0	0.54
	1.80721	0.73945	0.292_7	0.59
	2.08163	0.54188	0.318_1	0.70
	2.38295	0.35329	0.340_3	0.71
	2.67364	0.19177	0.377_2	0.24
1.72014	0.53374	2.07208	0.160_8	0.16
	0.89719	1.61294	0.189_2	0.39
	1.22304	1.25568	0.226_6	0.42
	1.54343	0.95580	0.261_8	0.59
	1.80770	0.73965	0.289_3	0.73
	2.08179	0.54193	0.314_7	0.81
	2.38235	0.35320	0.337_2	0.79
	2.67368	0.19177	0.370_2	0.35
1.66148	0.54735	1.90036	0.199_0	−0.65
	0.89133	1.48245	0.227_7	−0.57
	1.18704	1.17111	0.262_2	−0.53
	1.48276	0.89247	0.308_5	−0.78
	1.75821	0.67393	0.340_8	−0.62
	1.99480	0.50719	0.369_8	−0.57
	2.29072	0.33740	0.369_0	0.23
	2.61563	0.15471	0.469_5	−0.78
1.65133	0.50384	1.95600	0.177_3	−0.06
	0.85360	1.53458	0.198_2	0.42
	1.15968	1.19063	0.251_7	−0.17
	1.46642	0.90810	0.288_3	−0.05
	1.71645	0.70231	0.323_0	−0.13
	1.98236	0.51604	0.346_3	0.12
	2.27509	0.33730	0.366_6	0.30
	2.55028	0.18292	0.427_6	−0.34
1.52498	0.49139	1.70606	0.213_2	−0.43
	0.80679	1.34184	0.245_0	−0.40
	1.08153	1.06701	0.276_1	−0.24
	1.35470	0.81539	0.324_8	−0.59
	1.60557	0.61542	0.365_3	−0.74
	1.82688	0.46450	0.389_6	−0.56
	2.09572	0.30871	0.398_8	−0.03
	2.40353	0.14216	0.486_1	−0.70
1.16782	0.58872	0.99294	0.330_0	−1.06
	0.79884	0.80461	0.347_5	−0.72
	0.99409	0.64322	0.372_5	−0.54
	1.21426	0.48665	0.379_2	0.19
	1.40921	0.35518	0.409_0	0.14
	1.62676	0.23288	0.404_0	0.65
	1.87534	0.10024	0.496_9	−0.23
1.08472	0.37254	1.09560	0.288_5	−0.29
	0.68320	0.81449	0.294_7	0.74
	0.89775	0.60861	0.401_8	−1.05
	1.11795	0.45023	0.417_3	−0.50
	1.38310	0.28338	0.437_1	−0.04
	1.62650	0.14437	0.531_8	−0.74
0.97360	0.33073	0.97264	0.305_8	−0.23
	0.60764	0.72441	0.324_0	0.37
	0.81048	0.54945	0.386_0	−0.23
	1.00721	0.40563	0.414_2	−0.10
	1.24238	0.25455	0.452_9	−0.11
	1.46512	0.13005	0.530_4	−0.56
0.85712	0.28895	0.84976	0.303_5	0.14
	0.53325	0.63573	0.329_7	0.57
	0.72015	0.48821	0.349_7	0.89
	0.89362	0.35989	0.389_8	0.65
	1.10740	0.22689	0.395_0	0.97
	1.29838	0.11525	0.498_0	−0.11
	D-Glucose–TMAB–Water			
1.91152	0.48715	1.96769	0.158_1	−1.00
	0.93162	1.68599	0.092_5	0.52
	1.33629	1.39716	0.094_4	0.00
	1.78118	1.09182	0.089_9	−0.20
	2.15133	0.83482	0.092_3	−0.42
	2.48582	0.61450	0.085_7	−0.08
	2.79602	0.40039	0.097_8	−0.25
	3.14369	0.18392	0.087_1	0.11
1.70685	0.44492	1.76339	0.102_4	0.55
	0.83753	1.47662	0.104_7	0.26
	1.17620	1.23765	0.103_1	0.07
	1.59513	0.94465	0.106_6	−0.09
	1.91060	0.74199	0.094_2	0.66
	2.22795	0.51261	0.122_7	0.05
	2.50445	0.33584	0.128_6	0.26
	2.76084	0.17256	0.167_6	−0.17
1.68047	0.52713	1.66379	0.111_7	0.28
	1.04867	1.28887	0.109_0	−0.08
	1.47862	0.98701	0.111_8	−0.28
	1.85253	0.73013	0.117_5	−0.17
	2.17128	0.51619	0.126_5	0.02
	2.55559	0.26705	0.153_7	−0.05
1.64520	0.43052	1.69558	0.098_2	0.63
	0.80845	1.41666	0.106_7	0.20
	1.11714	1.20543	0.097_2	0.40
	1.50432	0.93028	0.106_4	0.07
	1.81728	0.71551	0.111_7	0.19
	2.11276	0.51668	0.120_4	0.34
	2.37423	0.34799	0.128_4	0.47
	2.60853	0.19767	0.162_2	0.04
1.41469	0.43669	1.27833	0.136_3	−0.41
	0.86934	1.06847	0.127_9	−0.60
	1.22748	0.81937	0.131_1	−0.51
	1.53933	0.60669	0.142_4	−0.29
	1.80924	0.43012	0.154_3	0.02
	2.13236	0.22282	0.211_2	−0.39
1.18671	0.36223	1.14330	0.143_8	−0.58
	0.72168	0.88698	0.138_1	−0.72
	1.01798	0.67953	0.150_8	−0.77
	1.27600	0.50291	0.173_4	−0.77
	1.50770	0.35843	0.177_4	−0.17
	1.77647	0.18563	0.271_8	−0.96
1.03352	0.23036	1.05712	0.092_4	0.25
	0.48086	0.87825	0.104_1	0.17
	0.71980	0.71322	0.107_6	0.34
	0.93200	0.57014	0.112_4	0.62
	1.12111	0.44379	0.125_3	0.72
	1.33817	0.30535	0.138_3	0.87
	1.51967	0.19509	0.152_8	0.80
	1.63203	0.12882	0.176_6	0.49
0.82982	0.18159	0.83330	0.135_8	−0.21

Table 1. (Continued)

m_R[a)]	m_1	m_2	Δ/m_1m_2	Diff.%
	0.37979	0.69364	0.135_5	−0.26
	0.56942	0.56421	0.137_3	−0.11
	0.73869	0.45188	0.142_2	0.11
	0.89047	0.35249	0.157_7	0.15
	1.06446	0.24289	0.182_4	0.11
	1.21713	0.15625	0.170_0	0.52
	1.30755	0.10321	0.209_1	0.16
0.78509	0.19603	0.77297	0.088_0	0.30
	0.52910	0.54012	0.129_6	0.10
	0.67487	0.43953	0.156_4	−0.15
	0.84104	0.33489	0.151_7	0.31
	1.00853	0.22766	0.192_5	−0.01
	1.12271	0.15532	0.265_2	−0.65
	1.22800	0.09720	0.301_2	−0.60

a) Reference solute is sodium chloride except for b). b) Reference solute is TBAB.

Table 2. The values of g_{ij} in Eq. 6

	D-Glucose–TBAB–Water	D-Glucose–TMAB–Water
g_{01}	0.47840	0.27828
g_{11}	0.09192	−0.06649
g_{02}	−0.12984	−0.19866
g_{21}	−0.05170	0.06080
g_{12}	−0.04619	0.05685
g_{03}	0.02332	0.10087
g_{31}	0.00500	−0.01642
g_{22}	0.01359	−0.01939
g_{13}	0.00393	−0.02080
g_{04}	−0.00175	−0.01707

Table 3. The values of h_{ij} *in* Eq. 10 for the system D-glucose–TBAB–water

h_{11}	1266.4
h_{21}	−52.9
h_{12}	−86.2
h_{31}	−13.5
h_{22}	23.7
h_{13}	−100.1

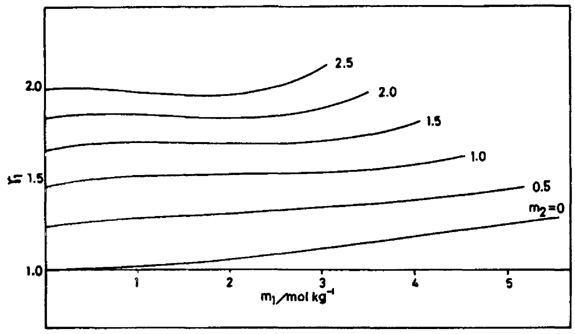

Fig. 1. Activity coefficients of D-glucose (γ_1) in aqueous TBAB solutions of various concentrations at 25 °C. m_1; Molality of D-glucose, m_2; molality of TBAB.

each solute increases in the presence of the other solute. Similar tendency was observed in the ternary system D-glucose–TMAB–water.

Heat of Dilution. Figure 3 shows the mean molar heat of dilution as a function of total concentration difference before and after dilution ($M-M'$). The values of molar heat of dilution for the binary systems, D-glucose–water and TBAB–water, obtained from this work agree with those of literatures.[15–17)] Using the least squares method, interaction parameters in Eq. 10 are calculated and are shown in Table 3.

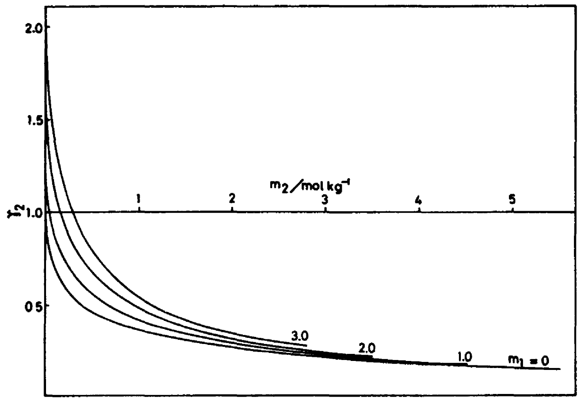

Fig. 2. Activity coefficients of TBAB (γ_2) in aqueous D-glucose solutions of various concentrations at 25 °C. m_1; Molality of D-glucose, m_2; molality of TBAB.

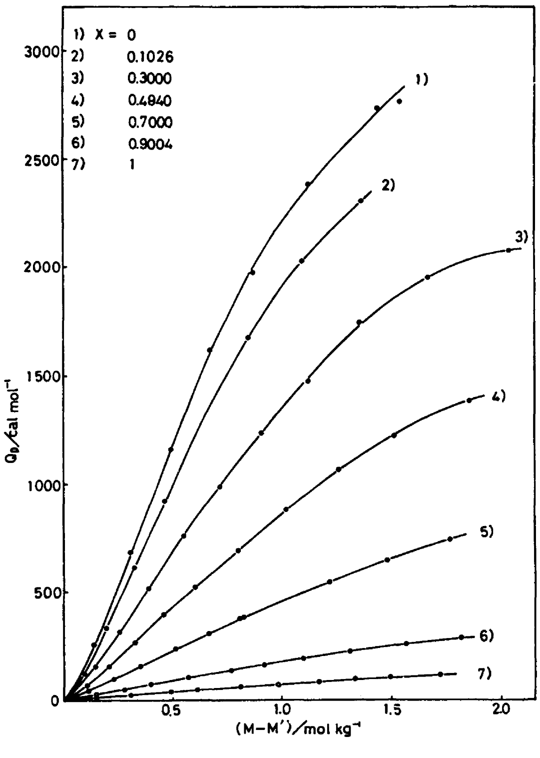

Fig. 3. Mean molar heat of dilution (Q_D) as a function of total concentration difference before and after dilution ($M-M'$) at 25 °C.
x; Mole fraction of D-glucose.

Discussion

As seen in Figs. 1 and 2, activity coefficient of each solute in ternary system increases in the presence of the other solute, showing mutual salting-out. Therefore, the repulsive force is working between these two solutes. Similar result, except for small in magnitude, was observed in the D-glucose–TMAB–water system. Taking into account the both solutes being strongly hydrated, the mutual salting-out observed in the D-glucose–TBAB–water system should be due to the structural salting-out arising from the structural difference of hydration cospheres around these two kinds of solutes.

Figures 4-(a) and -(b) show the relations between the changes of the excess thermodynamic quantities of mixing and the mole fraction of D-glucose at total molalities 1 and 2 mol kg^{-1}, repsectively. In these figures, the solid lines with star sign denote the excess free energy change of mixing for the D-glucose–TMAB–water system. The values of $\Delta_m G^{ex}$ for the both systems are positive, but the magnitude for the D-glucose–TBAB–water system is larger than that for the D-glucose–TMAB–water system. This result indicates that the hydrophobic hydration plays an important role on the magnitude of $\Delta_m G^{ex}$. The positive value of $\Delta_m G^{ex}$ implies that the system becomes unstable by mixing.

On the D-glucose–TBAB–water system, the positive value of $\Delta_m G^{ex}$ comes from the difference between large positive excess enthalpy change and entropy change, that is, the predominance of excess enthalpy term over excess entropy term makes $\Delta_m G^{ex}$ positive. Thus the unstableness of the system caused by mixing is due to the large positive excess enthalpy change.

Let us consider the mechanism of interaction between two kinds of solutes on the basis of the thermodynamic results obtained in this work. As stated in the introduction of this paper, both solutes are strongly hydrated but their structures of hydration cospheres are different each other. Accordingly the structural incompatibility causes the destruction of water structure around each solute, resulting in the increase of positive $\Delta_m S^{ex}$. The destruction of water structure accompanies the cleavage of hydrogen bonds among water molecules and makes the $\Delta_m H^{ex}$ value positive.

In order to compare the thermodynamic quantities of this system with those of the urea–TBAB–water system, thermodynamic transfer quantities were calculated by Eqs. 20, 21, and 22, and shown in Figs. 5 and 6 together with those for the urea–TBAB–water system reported by Wen *et al.*[18] As seen in Fig. 5, free energy ($\Delta\bar{G}_1^{tr}$), enthalpy ($\Delta\bar{H}_1^{tr}$), and entropy ($\Delta\bar{S}_1^{tr}$) of transfer of D-glucose from water to aqueous TBAB solution at infinite dilution are all positive, indicating the transfer process is disfavoured in enthalpic sence. The positive values of ΔH_1^{tr} and ΔS_1^{tr} mean the decrease of water structure around D-glucose in the transfer process. It is striking that the $T\Delta\bar{S}_1^{tr}$ *vs.* m_2 and $\Delta\bar{H}_1^{tr}$ *vs.* m_2 curves have maximum points around $m_2=1.5$, although the $\Delta\bar{G}_1^{tr}$ *vs.* m_2 curve gradually increases with m_2. The concentration of TBAB showing the maximum values of $\Delta\bar{H}_1^{tr}$ and $\Delta\bar{S}_1^{tr}$ nearly corresponds to the concentration at the minimum point observed in partial molar volume *vs.* concentration curve in aqueous TBAB solution.[19] At the concentration showing the minimum point, clusters around TBAB arrive at maximum cooperation in constructing a clathrate-like structure.[20] Therefore, this fact indicates that the water structure around D-glucose is destructed most strongly by TBAB at this concentration.

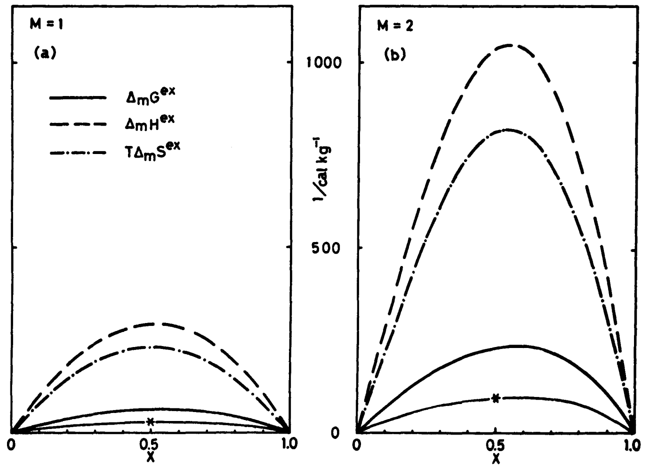

Fig. 4. Changes of excess thermodynamic quantities of mixing for the D-glucose–TBAB–water system at total molality (a) 1 or (b) 2 mol kg^{-1} at 25 °C. *x*; Mole fraction of D-glucose.

The solid lines with star sign denote change of excess free energy of mixing for the D-glucose–TMAB–water system.

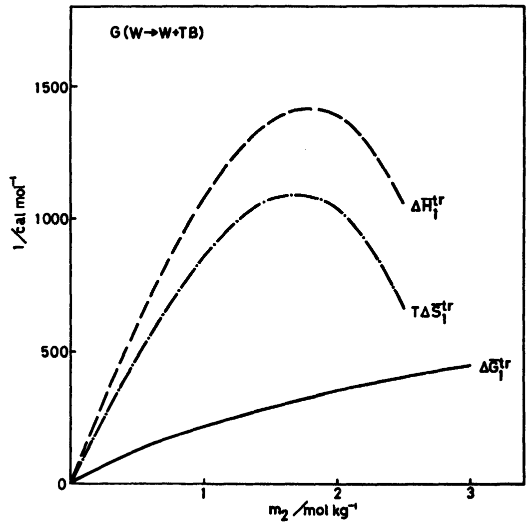

Fig. 5. Thermodynamic transfer functions of D-glucose from water to aqueous TBAB solution at infinite dilution at 25 °C.

m_2; Molality of TBAB.

Thermodynamic transfer functions of TBAB from water to aqueous D-glucose solution at infinite dilution are shown in Fig. 6-(a) as a function of the concentration of D-glucose. Similarly to Fig. 5, signs of all transfer functions are positive indicating that salting-out are caused by the large enthalpic contribution. Both positive $\Delta\bar{H}_2^{tr}$ and $\Delta\bar{S}_2^{tr}$ mean that the clathrate-like

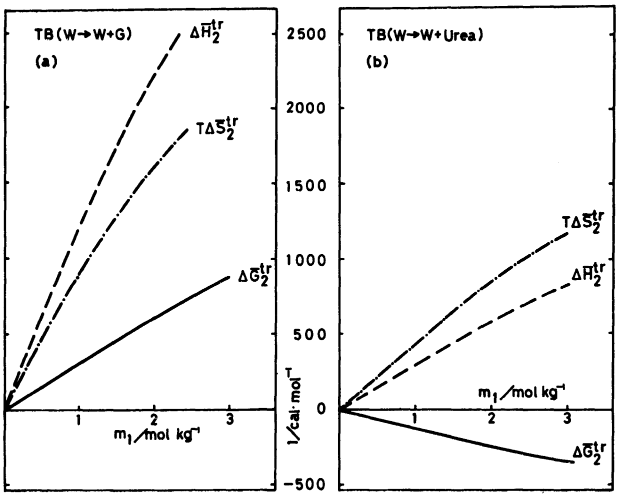

Fig. 6. Thermodynamic transfer functions of TBAB from water to (a) aqueous D-glucose solution or (b) aqueous urea solution[18)] at infinite dilution at 25 °C. m_1; Molality of D-glucose or urea.

structure of water around TBAB decreases in the presence of D-glucose. Figure 6-(b) shows the thermodynamic transfer functions of TBAB from water to various concentrations of aqueous urea solutions.[18)] Comparing Fig. 6-(a) with Fig. 6-(b), one can find that both $\Delta\bar{H}_2^{tr}$ and $\Delta\bar{S}_2^{tr}$ are positive in each system but their relative magnitudes are different, that is, $\Delta\bar{H}_2^{tr} > T\Delta\bar{S}_2^{tr}$ for the D-glucose–TBAB–water system while $\Delta\bar{H}_2^{tr} < T\Delta\bar{S}_2^{tr}$ for the urea–TBAB–water system. Thus $\Delta\bar{G}_2^{tr}$ for the urea–TBAB–water system is negative, indicating salting-in. The positive value of $\Delta\bar{S}_2^{tr}$ in these two systems indicate that both D-glucose and urea decrease the clathrate-like structure of water around TBAB, but D-glucose needs more energy to break down the hydrogen bonds in clathrate-like structure than urea does. We can not explain the detail mechanism of destruction of clathrate-like structure by D-glucose at the present stage. However, it is plausible that the incompatibility of structure of hydration cosphere around D-glucose and that around TBAB enforces the mutual structure breaking action, because both solutes are known to be structure makers.

The conclusion drawn from the comparison of our results with Wen's results is that hydrophobic hydration is destabilized in the presence of both D-glucose (hydrophilic structure maker) and urea (hydrophilic structure breaker).

Saccharides and polyalcols are known to stabilize the native conformation of protein in aqueous solution, while urea destabilizes it. Hydrophobic interactions are considered to play an important role for the maintenance of the native conformation of protein.[21)] The positive value of $\Delta\bar{G}_2^{tr}$ in aqueous D-glucose solution suggests that the hydrophobic moieties of protein may be more unstable in aqueous D-glucose solution than in water. Therefore, the salting-out effect of D-glucose for the hydrophobic TBAB may be related to the stabilization of native conformation of protein in aqueous D-glucose solution.

In conclusion, the excess enthalpy change ($\Delta_m H^{ex}$) and the excess entropy change ($\Delta_m S^{ex}$) of mixing for the ternary system D-glucose–TBAB–water are positive, showing that the degree of hydration of each solute in ternary solution decreases as compared with that in binary solution. The positive value of $\Delta_m G^{ex}$ which originates from the difference between $\Delta_m H^{ex}$ and $T\Delta_m S^{ex}$ indicates that each binary solution is more stable than the mixed ternary solution. Enthalpy and entropy changes of transfer of TBAB from water to D-glucose solution are positive similarly to those from water to urea solution. However, free energy of transfer of TBAB from water to D-glucose solution is positive in contrast to the case of urea–TBAB–water system. These differences seem to reflect the difference of structural effect between D-glucose and urea.

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