of the length of the chain,[40] and this value was also found for PAA, PEI, and its analogs. On the other hand, the P_{2p} of PSt and PP were -6.0 and 0, respectively, being larger than -20. These large P_{2p} values suggested that the PSt and PP ions had the strong interactions with water molecules by π electrons of the benzene ring and the phosphate group, respectively. Similarly, the comparatively large P_{2p} value of PGA sug-

gests the strong contribution of the interactions from hydrogen bonds and π electrons mentioned above. At full degree of neutralization, the PGA ion was found to be hydrated by three water molecules per monomer unit from the E_{2p} by the same method as that of the previous paper.[22] The extent of the electrostriction of PGA ions is seen to be about the same as that of PAA ions likewise having carboxyl groups.

(40) W. L. Masterton, *J. Chem. Phys.*, 22, 1830 (1954).

Mean and Single-Ion Activity Coefficients and Transference Data of the Sodium Salt of a Deoxyribonucleic Acid in Aqueous Solution[1]

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ABSTRACT: The mean activity coefficient of the sodium salt of a deoxyribonucleic acid, NaDNA, in two- and three-component systems, *i.e.*, NaDNA + H_2O, and NaDNA + NaCl + H_2O, was investigated by the emf method. The transference and related measurements were also carried out for the determination of the net valency and the transference number of DNA anions. The polymer charge fraction, f_{2p}, was concentration insensitive, decreased with increasing concentration of added salt, and was larger in the denatured state than in the native one. The transference number of DNA anions in the NaDNA + H_2O system was about 0.5, being insensitive toward the polymer concentration. The mean activity coefficient of NaDNA increased sharply with polymer concentration (0.0007 ~ 0.003 equiv l.$^{-1}$), indicating the presence of the strong short-range interactions between DNA molecule and solvent water. A similar tendency was also noticed for the single-ion activity coefficient of DNA anions. The single-ion activity coefficient of gegenions slightly decreased with polymer concentration.

The solution properties of deoxyribonucleic acid (DNA) have been intensively investigated by using various experimental techniques, *i.e.*, light scattering,[2] viscosity,[3] sedimentation,[4] Donnan equilibrium,[5] electrophoresis,[6] etc. However, no measurement has been reported on the mean activity coefficient, which is one of the most fundamental thermodynamic quantities. We have measured this quantity for several synthetic polyelectrolytes by emf measurements of a concentration cell with transference,[7-9] and by isopiestic vapor pressure measurements.[10-15] Recently Dolar and Les-

kovsek[16] investigated the mean activity coefficients of polystyrenesulfonic acid by the emf method. In a previous paper,[17] sodium salts of poly(L-glutamic acid), NaPGA, were studied by the measurements of the mean and single-ion activity coefficients, osmotic coefficient, transference properties, and partial molal volume. The contribution of the short-range solvent–solute interactions on NaPGA properties was noted. In the present paper, we report the activity and transference data for sodium salts of native and denatured DNA in the binary and ternary systems, *i.e.*, NaDNA + H_2O and NaDNA + NaCl + H_2O, and compare the results with those previously obtained for synthetic polyelectrolytes. It should be noted that the present work is the first of a series of the thermodynamic investigations of DNA and its biological function from this laboratory. This work will be followed by the study of the catalytic action of DNA in ionic reactions (the primary salt effects), in which the information on the mean activity coefficient given in the present work is indispensable.

Experimental Section

Materials. The sodium salt of salmon sperm DNA (NaDNA) employed in these investigations was purchased from Calbiochem Corp., Los Angeles, Calif., U.S.A. (Lot. 50211). This material was purified by washing with 85% ethanol (the pH was adjusted to 7~8 by adding 0.001 N NaOH), then with pure ethanol, and pure acetone cooled to 0~5°. Then the NaDNA was dried for about 20 hr under

(1) (a) Presented at the 18th Annual Meeting of the Society of High Polymers, Japan, May 1969, Kyoto. (b) Supported in part by the Grant in Aid of the Ministry of Education.

(2) See, for example, P. Doty and B. H. Bunce, *J. Amer. Chem. Soc.*, 74, 5029 (1952); G. L. Brown, M. B. M'Ewen, and M. I. Pratt, *Nature*, 176, 161 (1955); J. Hermans, Jr., *J. Phys. Chem.*, 63, 175 (1959).

(3) See, for example, B. E. Conway and J. A. V. Butler, *J. Polym. Sci.*, 42, 441 (1960).

(4) See, for example, A. R. Peacocke and H. K. Schachman, *Biochim. Biophys. Acta*, 15, 198 (1954); K. V. Shooter and J. A. V. Butler, *Trans. Faraday Soc.*, 52, 734 (1956); P. F. Davison, *Proc. Nat. Acad. Sci. U. S.*, 45, 1560 (1959).

(5) See, for example, U. P. Strauss, C. Helfgott, and H. Pink, *J. Phys. Chem.*, 71, 2550 (1967).

(6) See, for example, P. D. Ross and R. L. Scruggs, *Biopolymers*, 2, 79 (1964).

(7) N. Ise and T. Okubo, *J. Phys. Chem.*, 69, 4102 (1965).

(8) N. Ise and T. Okubo, *ibid.*, 70, 1930 (1966).

(9) N. Ise and T. Okubo, *ibid.*, 70, 2400 (1966).

(10) N. Ise and T. Okubo, *ibid.*, 71, 1287 (1967).

(11) N. Ise and T. Okubo, *ibid.*, 71, 1886 (1967).

(12) T. Okubo, N. Ise, and F. Matsui, *J. Amer. Chem. Soc.*, 89, 3697 (1967).

(13) N. Ise and T. Okubo, *J. Phys. Chem.*, 72, 1361 (1968).

(14) N. Ise and K. Asai, *ibid.*, 72, 1366 (1968).

(15) N. Ise and T. Okubo, *ibid.*, 72, 1370 (1968).

(16) D. Dolar and H. Leskovsek, *Makromol. Chem.*, 118, 60 (1968).

(17) N. Ise and T. Okubo, *Macromolecules*, 2, 401 (1969).

TABLE I

TRANSFERENCE AND RELATED DATA IN TERNARY SYSTEMS NaDNA + NaCl + H_2O SYSTEMS AT 25°

Sample	$10^3 m_2$, equiv/ 1000 g	pH	$10^4 \kappa$, mho cm^{-1}	$10^5 N_e$, equiv	$10^5 Q_{2p}$, equiv	f_{2g}	f_{2p}	t_{2g}	t_{2p}	U_{2p}, cm^2 V^{-1} sec^{-1}
Denatured DNA, $m_3 = 0$	0.719	8.15	0.498	0.280	0.218	0.67	0.67	0.48	0.52	3.7_5
	0.958	8.17	0.655	0.373	0.304	0.65	0.65	0.47	0.53	3.7_7
	1.44	8.20	0.945	0.560	0.441	0.65	0.65	0.49	0.52	3.5_1
	1.92	8.25	1.25	0.746	0.581	0.66	0.66	0.49	0.51	4.4_5
	2.16	8.36	1.38	0.839	0.635	0.66	0.66	0.50	0.50	3.3_1
	2.30	8.52	1.47	1.03	0.748	0.67	0.67	0.51	0.49	3.2_4
	2.87	8.54	2.03	1.22	1.00	0.66	0.66	0.45	0.55	4.0_2
Native DNA, $m_3 = 0.001$	0.755	8.48	1.51	0.653	0.188	0.72	0.34	0.41	0.10	2.0_2
	1.01	8.65	1.61	0.746	0.270	0.67	0.35	0.41	0.13	2.0_8
	1.51	9.00	1.81	0.746	0.313	0.63	0.39	0.42	0.16	2.0_3
	2.01	9.30	2.00	0.870	0.445	0.59	0.38	0.43	0.20	2.0_1
	2.26	9.52	2.13	0.920	0.525	0.58	0.39	0.43	0.22	2.1_6
	2.41	9.57	2.18	1.020	0.593	0.57	0.39	0.43	0.23	2.1_3
	3.02	9.58	2.43	1.244	0.761	0.56	0.42	0.44	0.26	2.1_4
Denatured DNA, $m_3 = 0.001$	0.604	8.29	1.56	0.653	0.136	0.82	0.53	0.41	0.11	2.9_8
	0.755	8.26	1.65	0.746	0.171	0.81	0.56	0.42	0.13	2.9_2
	1.01	8.03	1.58	0.771	0.269	0.67	0.56	0.41	0.12	2.9_6
	1.51	8.56	2.08	0.746	0.276	0.74	0.57	0.43	0.21	3.0_0
	2.01	8.89	2.35	0.870	0.369	0.71	0.57	0.44	0.24	2.9_3
	2.26	9.11	2.51	0.920	0.440	0.69	0.56	0.44	0.27	3.0_7
Native DNA, $m_3 = 0.003$	0.677	8.40	3.88	1.74	0.160	0.88	0.33	0.40	0.03	1.8_0
	1.35	8.69	4.14	2.49	0.384	0.81	0.38	0.41	0.06	1.8_4
	1.81	9.01	4.30	2.04	0.415	0.77	0.37	0.41	0.08	1.8_8
	2.03	9.15	4.41	1.99	0.675	0.75	0.38	0.41	0.09	2.0_3
	2.71	9.31	4.65	2.24	0.664	0.71	0.38	0.41	0.11	1.9_9
Denatured DNA, $m_3 = 0.003$	0.677	8.25	3.98	1.74	0.133	0.91	0.53	0.40	0.04	2.4_5
	1.35	8.19	4.31	1.99	0.298	0.85	0.51	0.41	0.08	2.5_3
	1.81	8.44	4.58	1.99	0.358	0.83	0.56	0.42	0.10	2.6_3
	2.03	8.51	4.70	1.99	0.409	0.82	0.55	0.42	0.11	2.6_9
	2.71	8.46	5.05	1.99	0.485	0.79	0.56	0.43	0.14	2.6_3

vacuum and stored in a refrigerator. The denaturation of NaDNA was accomplished by heating its solution for 10 min at 100°, and then cooling it rapidly in ice. The denaturation was checked by the hypochromism at 260 mμ. The water used to prepare solutions was ion exchanged with cation- and anion-exchange resins. All solutions were stored at 0~5°.

Transference Experiments. The principles of the transference experiments are based on the methods developed earlier by Huizenga, Grieger, and Wall,[18] and the details of the experiments have been described in previous papers.[19,20] An H-type glass tube divided into two compartments by a sintered-glass frit sealed at the center was used as the cell. The electrodes were bright platinum wire. The constant current was supplied by a regulated power supply of the Kikusui Electronics Corp., Tokyo (Model 722c), in a range of 0.1 × 10^{-3} to ~0.4 × 10^{-3} A, and the field strength was between 2 and 4 V cm^{-1}. After electrolysis, the determination of the DNA concentration was carried out after denaturation treatment by using a Hitachi spectrophotometer, Model EPS-3T. The optical density was measured at 260 mμ. The electric conductivity of the solution was measured by using Jones and Ballinger types of cells[21] and a Wheat-

(18) J. R. Huizenga, P. F. Grieger, and F. T. Wall, *J. Amer. Chem. Soc.*, **72**, 2636 (1950).

(19) T. Okubo, Y. Nishizaki, and N. Ise, *J. Phys. Chem.*, **69**, 3690 (1965).

(20) N. Ise and T. Okubo, publication in preparation.

(21) G. Jones and M. Ballinger, *J. Amer. Chem. Soc.*, **53**, 411 (1931).

stone bridge at 1000 cps. The pH measurements were performed by using a Horiba Model P pH meter. The experiments were carried out in a thermostat at 25 ± 0.02°.

Activity Coefficients. The details of the measurements of the mean activity coefficient were described in the previous paper.[7] A concentration cell with transference was set up with sodium glass electrodes
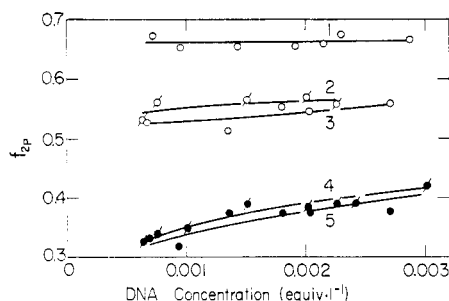
Na glass electrode	NaDNA solution 2	NaDNA solution 1	Na glass electrode	(I)
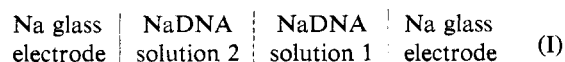
The emf (E) of the cell is given by

$$E = \frac{(1 + \alpha)RT}{\alpha F} \int_{a_2}^{a_1} t_{2p} d \ln a \qquad (1)$$

where a_1 and a_2 are the mean activities of polyelectrolyte in solutions 1 and 2, respectively, R the gas constant, T the temperature, F the Faraday charge, t_{2p} the transference number of macroions, and α the number of free gegenions dissociated from one macroion. By combining the transference number and the emf data, the mean activity coefficient, γ_α, can be determined.

The cell used to obtain the single-ion activity of sodium ions was

Na glass electrode | NaDNA solution | calomel electrode

(II)
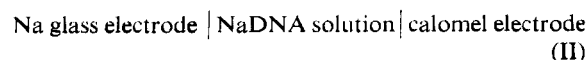
Assuming that the liquid junction potential between KCl solution in the calomel electrode and the sample solution

Figure 1. Polymer charge fraction of NaDNA in ternary and binary aqueous solutions at 25°: curve 1, denatured, $m_3 = 0$; 2, denatured, $m_3 = 0.001$; 3, denatured, $m_3 = 0.003$; 4, native, $m_3 = 0.001$; 5, native, $m_3 = 0.003$.

does not vary with the concentration of the sample, the emf (E) can be expressed as

$$E = E_0 - \frac{RT}{F} \ln a_{2g} \qquad (2)$$

where E_0 is the standard emf of the above cell, and a_{2g} the single-ion activity of the gegenions, *i.e.*, Na^+ in the present case. The sodium glass electrodes used in cells I and II are products of the Horiba Manufacturing Co., Kyoto, Japan. The measuring circuit consisted of a precision potentiometer (Type K2 of Shimazu Manufacturing Co., Kyoto) and a vibrating reed electrometer (TR-84MS) manufactured by Takeda Riken Industry Co., Tokyo).

Results and Discussion

The transference and related data of NaDNA under various conditions are compiled in Table I. The symbols are defined as follows: κ, total specific conductivity minus solvent specific conductivity; m_2, polymer concentration in equivalents per liter; m_3, molarity of NaCl; N_e, total equivalents of electricity; Q_{2p}, increase in equivalents of DNA anions in anode compartment; f_{2g}, fraction of sodium ions not associated with DNA anion; f_{2p}, polymer charge fraction; t_{2g}, transference number of sodium ion; t_{2g}, transference number of DNA anions; U_{2p}, macroion mobility defined by $\kappa_{2p}f_{2p}/m_{2p}F$. As is clearly seen from Figure 1 and Table I, the results show that (1) the polymer charge fraction f_{2p} is rather insensitive toward polymer concentration, (2) the f_{2p} of denatured DNA (coiled state) is markedly larger than that of native DNA (helical state), *i.e.*, the gegenion association of the native DNA is stronger than that of the denatured DNA, and (3) f_{2p} decreases with increasing concentration of the added salt (NaCl). The native DNA in pure water is not stable at room temperature,[22] and its f_{2p} in the binary system could not be determined.[23] The same result as 1 was found for other polyelectrolytes and has been discussed previously in detail.[20] The fact that the denatured DNA has larger f_{2p} values than the native one is easily accounted for if one takes into consideration the higher charge density in the he-
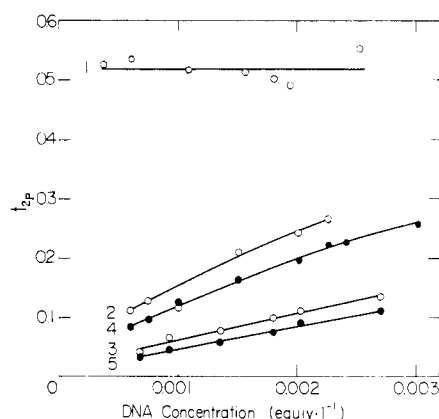

Figure 2. Transference number of DNA ions in ternary and binary aqueous solutions at 25°: curve 1, denatured, $m_3 = 0$; 2, denatured, $m_3 = 0.001$; 3, denatured, $m_3 = 0.003$; 4, native, $m_3 = 0.001$; 5, native, $m_3 = 0.003$.

lical state. The tendency of f_{2p} to decrease with increasing concentration of added salt was observed by Wall and Eitel,[24] and by us[20] for the sodium polyacrylate (NaPAA) + NaCl + H_2O system.[25, 26]

The fraction of sodium ions not associated with macroion, f_{2g}, shows similar tendencies as f_{2p} except for the polymer concentration dependence. The values of f_{2g} at $m_3 = 0$ did not change with the polymer concentration, whereas those at $m_3 = 0.001$ and 0.003 decreased, as is shown in Table I.

The transference number of DNA anions, t_{2p}, is shown in Figure 2 for various salt concentrations and conformations. It should be noted that the t_{2p} values in the ternary systems (curves 2∼5) are much lower than those in the binary system (curve 1). This is due to the predominant contribution of added salt to the electric conductivity of the solution. The t_{2p} values in the binary system are about 0.5 and are in rough agreement with those found for sodium polyacrylate.[19] This agreement is rather peculiar if one takes into consideration the bulkiness of DNA molecules, *i.e.*, the fact that the molecular weight of DNA per dissociable ionic group is estimated to be 370, and the native DNA may be assumed to be a cylinder having a radius of 11.4 Å.[27] Furthermore the observed mobility of DNA anions (Table I) are not smaller and in fact even larger than those of typical polyelectrolytes, *e.g.*, NaPAA, sodium poly(styrene sulfonate) (NaPSt), and sodium poly(L-glutamate) (NaPGA), which have mobilities of 1∼2 × 10^{-4} cm^2 V^{-1} sec^{-1} at 25°.[20] The decisive interpretation for these transference and mobility behaviors is difficult, but the large f_{2p} value (≈ 0.67) certainly must be taken into consideration. The fact that the t_{2p} value of the denatured NaDNA in the ternary system is larger than that of the native NaDNA is understandable

(22) See, for example, C. Schildkraut and S. Lifson, *Biopolymers*, 3, 195 (1965); K. Hamaguchi and E. P. Geiduschek, *J. Amer. Chem. Soc.*, 84, 1329 (1962). See also R. B. Inman and D. O. Jordan [*Biochim. Biophys. Acta*, 42, 421 (1960)], in which the stability of the native DNA was discussed by using transference data.

(23) The f_{2p} of the native DNA in pure water may be estimated from Figure 1 to be about 0.5 by comparison with the f_{2p} values of the denatured DNA.

(24) F. T. Wall and M. J. Eitel, *J. Amer. Chem. Soc.*, 79, 1556 (1957).

(25) Recently, Ross[26] determined the effectively charged fraction of DNA anions, *i*, by applying Gorin's equation to the data of the electrophoretic and membrane equilibrium measurements at 0°, and obtained an increasing tendency of *i* with increasing NaCl concentration. This result is not consistent with our observation. The reason for the discrepancy is not clear at present.

(26) P. D. Ross, *Biopolymers*, 2, 9 (1964).

(27) R. Lanridge, D. A. Marvin, W. E. Seeds, H. R. Wilson, C. W. Hooper, M. H. F. Wilkins, and L. D. Hamilton, *J. Mol. Biol.*, 2, 38 (1960).
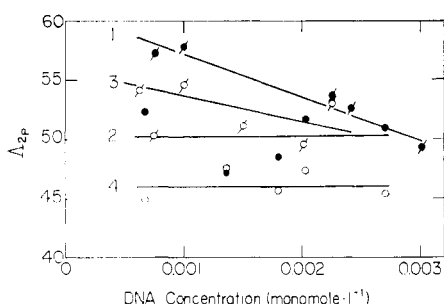
Figure 3. Equivalent conductance of DNA ions at 25°: curve 1, native, $m_3 = 0.001$; 2, native, $m_3 = 0.003$; 3, denatured, $m_3 = 0.001$; 4, denatured, $m_3 = 0.003$.

in the light of the f_{2p} values of the two conformations, for the f_{2p} of the native DNA is strikingly larger than that of the denatured DNA.

From the transference experiments, the equivalent conductance of the hypothetically fully dissociated macroions, Λ_{2p}, can be derived.[20] Figure 3 shows the Λ_{2p} values calculated for the native and denatured DNA in the presence of added salt ($m_3 = 0.001$ and 0.003). The figure shows that the helical DNA moves faster than the coiled one. This is clearly understandable since the rodlike native DNA would have a smaller frictional resistance than the expanded denatured DNA. From the Λ_{2p} values, one can calculate the mobility of macroions, U_{2p}, by the relation

$$U_{2p} = \kappa_{2p} f_{2p}/m_2 F = 10^{-3} f_{2p} \Lambda_{2p}/F \qquad (4)$$

where κ_{2p} is the macroion contribution to the specific conductivity and F the Faraday charge. The U_{2p} values of NaDNA ions thus obtained are given in Table I (the last column). It is seen that the U_{2p} values are larger for the coiled state than for the helix state, in contrast with the Λ_{2p} case. This result is due to the fact that the f_{2p} values of the denatured NaDNA are strikingly larger than those of the native one (see the ninth column of Table I). It should be noted, however, that the U_{2p} values observed by electrophoresis[28,29] were larger for the native state than for the denatured one, in contradiction with our results. The reason for this discrepancy is not clear at present; differences in the experimental conditions such as pH and concentrations of added salts might be responsible.

The essential data of the mean activity coefficients of the denatured NaDNA obtained from the emf of a concentration cell with transference are given in Table II. The first column gives the concentration of solution 2 in the cell II (equivalent per liter), that of solution 1 being the most concentrated solution. The γ_α values (in the last column of Table II) were the activity coefficients determined on the basis of a $\gamma_{2g,\alpha}$ value at $m = 0.001$ by the same convention as adopted in the previous papers.[6-8] The γ_α strikingly increased with increasing polymer concentration. This tendency was also observed for sodium salts of poly(vinyl alcohol) partially acetalized with glyoxylic acid (NaPVAG),[8] and for sodium polyphosphate (NaPP),[15] sodium poly(styrene sul

(28) L. Constantino, A. M. Liquori, and V. Vitagliano, *Biopolymers*, 2, 1 (1964).
(29) B. M. Olivera, P. Baine, and N. Davidson, *ibid.*, 2, 245 (1964).

TABLE II
MEAN ACTIVITY COEFFICIENT OF THE DENATURED
NaDNA IN PURE WATER AT 25°

Concn, equiv l.$^{-1}$	Emf,[a] mV	f_{2p}[b]	γ_α[c]
0.000719	8.11	0.523	0.95
0.000958	6.79	0.532	0.98
0.00144	4.45	0.515	1.24
0.00192	3.17	0.511	1.49
0.00216	2.28	0.499	1.95
0.00230	1.89	0.490	2.26
0.00287	0	0.549	3.33

[a] The emf measurements were carried out with $m_1 = 0.00287$. [b] From Table I of the present paper. [c] The γ_α values were determined using a $\gamma_{2g,\alpha}$ value at 0.001 equiv l.$^{-1}$

fonate) (NaPSt),[13] and others,[11,14,17] and is attributable to ion–solvent interactions such as hydrophobic, electrostrictional, π-electron interactions, etc. Thus, it is highly probable that the DNA molecule interacts strongly with solvent molecules, since the increasing tendency of γ_α is observed in a range of highly dilute concentrations, in which most of the synthetic polyelectrolytes show a decreasing trend of γ_α. The DNA molecule is composed of monomer units (mononucleotides) having three groups—phosphate, ribose, and base. The phosphate groups can interact strongly with water by charge-transfer-type interactions as was discussed on the basis of the osmotic and mean activity coefficients for polyphosphate.[16] Ribose may also interact with water through a hydrogen bond by its OH groups, which is one factor that prevents the formation of icebergs in water. This has been suggested both from the solubility of naphthalene in aqueous solutions of soluble starch,[30] and from the mean activity coefficients of carboxymethylcellulose.[31] These polymers are quite similar to the ribose and give rise to only weak hydrophobic interaction with water. Furthermore, the nitrogen atoms in the four kinds of bases, *i.e.*, adenine, guanine, cytosine, and thymine, can interact strongly with water molecules by hydrogen bond formation. Thus all three groups in the mononucleotides interact with water, and do not have strong hydrophobic effect on water structure. The polymer concentration dependence of γ_α of the denatured DNA, therefore, is quite logical.

The single-ion activity coefficient of the sodium ions of the denatured NaDNA was measured, though its physical meaning is very obscure.[32,33] The stoichiometric and thermodynamic single-ion activity coefficients of gegenions are denoted by $\gamma_{2g,z}$ and $\gamma_{2g,\alpha}$ respectively, and are interrelated to one another by

$$\gamma_{2g,z} = f_{2g} \gamma_{2g,\alpha} \qquad (5)$$

where f_{2g} denotes the fraction of effectively disassociated gegenions, and can be determined by the transference measurements. The definitions of these two coefficients were given in the previous paper.[19] The obtained results are given in Table III. Both $\gamma_{2g,z}$ and $\gamma_{2g,\alpha}$ are observed to decrease slightly with increasing DNA concentration.

(30) T. Okubo and N. Ise, *J. Phys. Chem.*, 73, 1488 (1969).
(31) N. Ise, K. Asai, and K. Takaya, publication in preparation.
(32) E. A. Guggenheim, *J. Phys. Chem.*, 33, 842 (1929).
(33) N. Ise and T. Okubo, *ibid.*, 70, 3025 (1966).

TABLE III

SINGLE-ION ACTIVITY COEFFICIENT OF SODIUM IONS
OF DENATURED NaDNA IN PURE WATER AT 25°

Concn, equiv l.$^{-1}$	Emf, mV	a_{2g}	$\gamma_{2g,z}$	$\gamma_{2g,\alpha}$
0.000719	154.9	0.000512	0.71_3	1.06_1
0.000958	152.0	0.000601	0.62_7	0.96_0
0.00144	145.8	0.000853	0.59_4	0.90_8
0.00192	140.6	0.00110	0.57_4	0.87_5
0.00216	138.5	0.00124	0.57_5	0.87_3
0.00230	137.0	0.00134	0.58_3	0.86_8
0.00287	132.3	0.00167	0.58_1	0.87_5

This concentration dependence is in a sharp contrast with that of the mean activity coefficients. Recently Lyons and Kotin[34] measured $\gamma_{2g,z}$ of denatured calf-thymus NaDNA by using ion-exchange membrane electrodes in pure water, and reported similar values as ours. The measurements of $\gamma_{2g,z}$ of NaDNA were also reported by Ascoli, *et al.*[35]

Next, let us consider the single-ion activity of the macroions. The mean activity coefficient, γ_α, is given by

$$\gamma_\alpha^{1+\alpha} = \gamma_{2g,\alpha}^\alpha \, \gamma_{2p,\alpha} \qquad (6)$$

where $\gamma_{2p,\alpha}$ is the thermodynamic single-ion activity coefficients of macroions, and α is the effective valency of a macroion, which can be determined by using the transference data. Figure 4 presents log $\gamma_{2p,\alpha}$ divided by α together with log γ_α and log $\gamma_{2g,\alpha}$. Since the value of $\gamma_{2p,\alpha}^{1/\alpha}$ sharply increases with polymer concentration, as is seen from the figure, the single-ion activity of DNA anion, a_{2p}, should increase at an enormous rate with the polymer concentration. The rapid increase of the single-ion activity of macroions was also observed for poly(L-glutamate) (PGA) ions in comparatively concentrated regions, and was accounted for by strong

(34) J. W. Lyons and L. Kotin, *J. Amer. Chem. Soc.*, **86**, 3634 (1964).
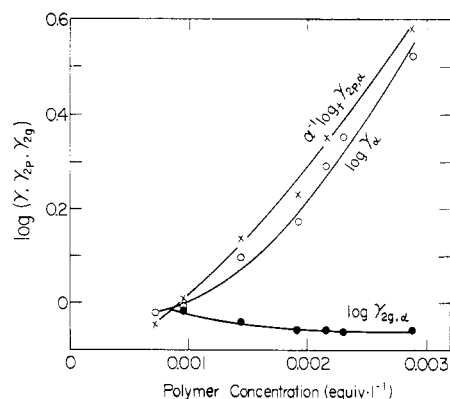(35) F. Ascoli, C. Botré, and A. M. Liquori, *J. Mol. Biol.*, **3**, 202 (1961).

Figure 4. Mean and single-ion activity coefficients of NaDNA at denatured state at 25°.

short-range interactions between PGA anions and solvent water molecules by hydrogen bond and/or π electron interactions. The a_{2p} of several typical synthetic polyelectrolytes other than NaPGA, however, sharply decreased with polymer concentration; for example, NaPAA and sodium salts of poly(vinyl alcohol) partially acetalized with glyoxylic acid (NaPVAG).[36] This concentration dependence of a_{2p} was attributed to an intermacroion linkage, which had resulted from strong electrostatic interactions.[36] The rapid increase of a_{2p} of DNA indicates the predominant contribution of short-range interactions between solvent and DNA.

From the above statement, it is seen that the concentration dependence of the mean activity coefficient of NaDNA suggests strong solvent–solute interactions. From the mean activity coefficients only, however, it cannot definitely be ascertained what kinds of solvent–solute interactions exist and which is the dominant one. To clarify this point, further study is in progress in this laboratory.

(36) N. Ise and T. Okubo, *J. Phys. Chem.*, **70**, 2407 (1966).