NMR Relaxation Studies for Sodium and Potassium Ions and Water Molecules in Concentrated Aqueous Solutions of Dibutyl Phosphate

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The hydration and alkali-ion binding of an aggregate of the dibutyl phosphate (DBP) ion in its isotropic aqueous solution were investigated by measuring the nuclear magnetic relaxation times for ^{17}O of H_2O, and ^{23}Na and ^{39}K of hydrated alkaline metal ions at various temperatures. The relaxation rates for the ^{17}O of H_2O showed that the rotational motion of the water molecule is more restricted in the sodium system than that in the potassium system. Arrhenius plots also showed that the activation energy for the relaxation rate of the water molecule is larger in the sodium system. The dependences of the longitudinal relaxation rates for the alkali ions on the DBP concentrations in these systems showed that the sodium ion has an enhanced tendency, over the potassium ion, to interact with the dibutyl phosphate ion and to form ion-aggregates.

Viscosity measurements showed that the appreciable restriction of the motion of the water molecules in DBP solutions corresponds to a great extent in the aggregation of DBP.

The formation of a liquid crystal was detected above 3 mol dm^{-3} at 25 °C for an aqueous dibutyl sodium phosphate solution.[1] The reorientation of water molecules was studied through the ^1H and ^2H longitudinal relaxation times (T_1) and the ^{17}O transverse relaxation time (T_2) determined from the linewidth. The molecular order parameters for water were also obtained from ^1H dipolar coupling and the quadrupolar splitting observed for ^2H and ^{17}O NMR.[2] The results were consistent with a model in which water molecules anisotropically reorient about an axis located in the H–O–H bisector plane and directed to a sodium ion site. Since the short-chain amphiphile of this system provides one of the simplest lyotropic mesophases, studies of this liquid crystalline system are expected to provide fundamental information concerning the structure and dynamics of ion aggregates. This system will also be appropriate for us to study the effects of metal ions on the formation of ion aggregates, since DBP strongly interacts with metal ions and is used as a reagent for metal-ion extraction.[3]

In the present study, the dynamics of water molecules and hydrated sodium or potassium ions were measured in highly concentrated and isotropic aqueous DBP solutions by using NMR relaxation and viscosity measurements. Our attention is focused on the differences between the sodium and the potassium salt regarding the properties of their isotropic aqueous solutions. Their microscopic behavior, obtained from the NMR studies, was related to their macroscopic behavior from viscosity measurements. The situation regarding the formed aggregates is expected to be understood through the dynamic behavior of the alkaline ions or water molecules. The NaDBP and KDBP systems were studied in the concentration range from 0.8 mol kg^{-1} to the highest concentration (around 11 mol kg^{-1}) of the isotropic solution, because Chachaty *et al.*[1] have shown that the critical micelle concentration in the NaDBP system is around 0.8 mol kg^{-1} at 25 °C and that the aggregation number of the amphiphile in each micelle is nearly constant from 1 to 3 mol kg^{-1} at 25 °C.

Experimental

Materials. Dibutyl hydrogenphosphate was supplied by Tokyo Kasei Ltd. It was neutralized by an aqueous sodium or potassium hydroxide solution and organic impurities were extracted out by benzene. After extraction, the aqueous solution was treated by Chelex 100 chelating resin to remove paramagnetic metal ions for NMR measurements; the solvent water was then evaporated. After the residual water of the crystal was removed by coevaporation with benzene, the crystal was kept in vacuo at 80 °C for one day. The purity and water content of the hygroscopic crystals were examined by ^1H NMR spectroscopy in 99.8% D_2O solution and Karl–Fischer's titration. The crystals, thus obtained, were $NaDBP\cdot 0.1H_2O$ and $KDBP\cdot 0.5H_2O$. The sodium nitrate, potassium nitrate, and potassium nitrite used were guaranteed reagents from Wako Pure Chemical Industries.

NMR Measurements. The ^2H, ^{17}O, ^{23}Na, and ^{39}K NMR spectra were obtained on a JEOL GX-270 FT NMR spectrometer operating at 41.5, 36.6, 71.5, and 12.6 MHz, respectively. The longitudinal relaxation time (T_1) was obtained by the inversion-recovery method, using the pulse sequence of $(-180°\text{ pulse-}t\text{-}90°\text{pulse-}T\text{-})_n$. For measurements of T_1, ten different pulse intervals (t) were used with a waiting time (T) of more than $10T_1$. The sample solution of DBP in 5% D_2O was bubbled with argon gas for about ten minutes just before each NMR measurement in order to remove any oxygen gas from the solution. The ^2H spectra were observed from 5% enriched ^2H_2O and ^{17}O from 0.5% enriched $H_2{}^{17}O$. The temperature of the sample solution was calibrated by a direct measurement for a solution in the NMR probe by using a digital surface thermometer over the temperature ranges studied.

Viscosity Measurement. The kinematic viscosity (ν) of each aqueous solution of DBPNa or DBPK salt was measured with a Canon–Fenske capillary viscometer at temperatures from 10 to 70 °C, controlled within 0.03 °C. The shear viscosity (η) was obtained from the relationship $\nu=\eta/\rho$, where the density (ρ) was measured by an Ostwald-type picnometer.

Results and Discussion

The phase diagram for the aqueous dibutyl sodium phosphate has been described by Chachaty et al. on the basis of the ^{2}H NMR spectra of deuterated water.[2] When the isotropic and liquid-crystal phases coexist, the ^{2}H NMR spectra of the water in the liquid crystal phase were observed as satellites of that in the isotropic one; we could thus calculate the percentage of water of the liquid-crystal phase from the peak area of the ^2H_2O NMR spectra in both phases. Some of the results are given in Fig. 1, where the potassium system is compared with the sodium system. The liquid-crystal region is much smaller for potassium salt than for sodium salt; for potassium salt, the liquid-crystal phase is always accompanied by the isotropic phase, and a transformation from the liquid-crystal to isotropic phase is easier in the potassium system than in the sodium system. This result suggests that aggregation including potassium ions occurred to a smaller extent than that including sodium ions in concentrated DBP aqueous solutions.

In order to determine the difference between the sodium and potassium ion in the formation of DBP aggregates in concentrated solutions, we measured the longitudinal relaxation times for ^{17}O of water, and ^{23}Na and ^{39}K, by varying the temperature and DBP concentration. This study covered the temperature range from 10 to 70 °C at 5 or 10 °C intervals and the concentration of the dibutylphosphate solutions from 0.8 to 11 mol kg^{-1}. Tables 1—4 show the relaxation rates obtained in the concentration range from 0.8 to 7.7 mol kg^{-1}. In an isotropic solution the longitudinal relaxation rate (R_1) for a quadrupolar nucleus ($I>1/2$) is given by Eq. 1[4]

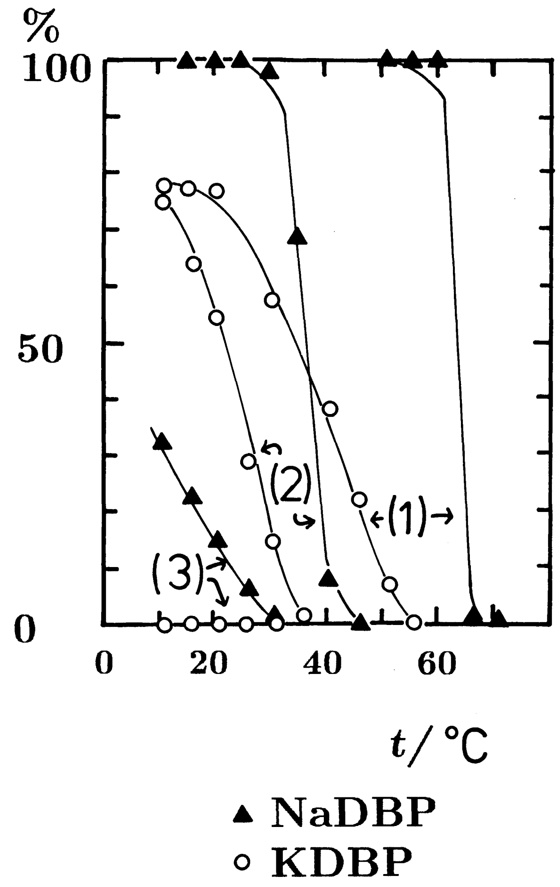

Fig. 1. Percentages of the water in the liquid crystal phase depending on the temperature for the sodium DBP and the potassium DBP aqueous solutions. The concentration is (1) 11 mol kg^{-1}, (2) 7.7 mol kg^{-1}, (3) 6.1 mol kg^{-1}.

Table 1. Concentration and Temperature Dependences of the Relaxation Rate R_1/s^{-1} for ^{17}O NMR of H_2O in the Sodium Dibutylphosphate Solutions in Comparing with That in the Concentrated Sodium Nitrate Solution[a,b)]

c/mol kg^{-1} t/°C	0.80	1.4	3.2	4.6	6.1	7.7	$NaNO_3$ (c=9.6)
10	562	690	1138	1634	2864		515
15	455	562	941	1299	2262		439
20	366	455	748	1033	1764		373
25	309	379	633	814	1437		317
29	254	316	521	676	1158		271
34	228	272	438	558	955		243
38	198	236	378	483	788	1075	211
43	174	206	328	412	683	889	187
47	156	181	282	355	602	766	168
56	123	146	213	269	446	580	140
66	98.7	119	170	213	333	427	113
ΔE_a(10—34)/kJ mol^{-1}	28	29	30	33	34	—	24
ΔE_a(38—66)/kJ mol^{-1}	22	21	25	26	28	28	19

a) All the values were obtained for the isotropic phase even if the liquid crystal phase coexists. b) Standard deviations for all the activation energies were within 1 kJ mol^{-1}.

Table 2. Concentration and Temperature Dependences of the Relaxation Rate R_1/s^{-1} for ^{17}O NMR of H_2O in the Potassium Dibutyl Phosphate Solutions Comparing with That for the Concentrated Potassium Nitrate or Nitrite Solutions[a,b)]

c/mol kg^{-1} t/°C	0.80	1.4	3.2	4.6	6.1	7.7	KNO_3 (c=4.0)	KNO_2 (c=10.0)
10	323	428	728	863	1406	2039		213
15	281	361	602	732	1192	1686		191
20	235	290	498	561	986	1380		172
25	202	255	433	493	791	1176		153
29	180	211	368	435	667	982		143
34	162	185	317	372	567	796		130
38	144	166	260	311	493	641	96.0	119
43	130	147	233	276	430	548	88.1	108
47	119	135	213	255	383	494	82.5	101
56	95.6	105	166	194	302	380	70.8	87.6
66	79.0	89.5	135	162	238	299	62.4	77.5
ΔE_a(10—34)/kJ mol^{-1}	22	26	25	25	28	28	—	15
ΔE_a(38—66)/kJ mol^{-1}	20	20	21	22	23	23	14	13

a) All the values were obtained for the isotropic phase even if the liquid crystal phase coexists. b) Standard deviations for all the activation energies were within 1 kJ mol^{-1}.

Table 3. Concentration and Temperature Dependences of the R_1/s^{-1} for the ^{23}Na Ion NMR in the Aqueous Sodium Dibutyl Phosphate Solutions Comparing with That for the Concentrated Sodium Nitrate Solution

c/mol kg^{-1} t/°C	0.80	1.4	3.2	4.6	6.1	7.7	NaCl (c=1.0)	$NaNO_3$ (c=5.0)	$NaNO_3$ (c=9.6)
10	57.7	93.4	173	288	505		23.6	53.8	76.9
15	52.4	79.7	151	246	421		21.8	46.3	64.9
20	45.5	69.1	130	209	355		20.1	41.5	55.6
25	42.4	59.8	113	197	314		18.4	35.3	48.3
29	35.8	52.9	99.0	161	267		16.6	30.9	41.5
34	33.9	47.8	88.2	146	236		15.4	28.2	36.6
38	30.9	44.1	80.4	131	215	357	14.3	25.6	32.9
43	27.0	39.8	72.5	121	193	337	13.4	23.1	30.1
47	25.0	36.6	66.4	112	172	295	12.7	21.2	27.2
56	21.9	32.1	58.3	91.1	147	246	11.4	18.3	23.0
66	19.4	28.7	52.6	79.5	126	213	10.4	16.2	19.8
ΔE_a(10—34)/kJ mol^{-1}	17	21	21	21	23	—	13	20	23
ΔE_a(38—66)/kJ mol^{-1}	14	13	13	16	17	17	10	15	17

a) All the values were obtained for the isotropic phase even if the liquid crystal phase coexists. b) Standard deviations for all the activation energies were within 1—2 kJ mol^{-1}.

$$R_1 = \frac{1}{T_1} = \frac{3\pi^2}{10}\left(\frac{e^2Q}{h}\right)^2 \frac{2I+3}{I^2(2I-1)} \int_0^\infty \langle V_{zz}(0)V_{zz}(t)\rangle \mathrm{d}t, \tag{1}$$

where eQ is the nuclear quadrupole moment, h Planck's constant, and $\langle\ \rangle$ an equilibrium ensemble average for a diagonal component of the electric field gradient tensor (V_{zz}). Here, it is convenient to use an effective correlation time (τ_{eff}), defined as

$$\tau_{\mathrm{eff}}\cdot\langle V_{zz}(0)\rangle^2 = \int_0^\infty \langle V_{zz}(0)V_{zz}(t)\rangle \mathrm{d}t. \tag{2}$$

Eq. 2 is useful when $1/\tau_{\mathrm{eff}}$ is much larger than ω_0, the nuclear precession frequency, where the exponential relaxation is observed and the relaxation rate (R_1), is independent of the frequency (ω_0), an extreme narrowing condition. It has been shown for many amphiphilic systems that this condition as well as the Lorentzian line shape is fulfilled for counterions and water molecules.[5)] It has been confirmed that these conditions also hold for ^{2}H and ^{17}O relaxation in this system;[2)] we verified this for the relaxation of ^{23}Na ions, even under the most viscous condition (6.1 mol kg^{-1} at 10 °C); that is, the relaxation time obtained at 71.5 MHz nearly coincided (within 5% error) with that measured at 23.8 MHz. We can, thus, write the relaxation time (T_1) of Eqs. 1 and 2 as

$$\frac{1}{T_1} = R_1(\omega_0) = \frac{3\pi^2}{10}\frac{2I+3}{I^2(2I-1)}\left(\frac{e^2Q\langle V_{zz}(0)\rangle}{h}\right)^2 \tau_{\mathrm{eff}}. \tag{3}$$

In order to interpret the relaxation data for a system

Table 4. Concentration and Temperature Dependences of the R_1/s^{-1} for the ^{39}K NMR in the Aqueous Potassium Dibutyl Phosphate Solutions Comparing with That for the Concentrated Potassium Nitrate or Nitrite Solution[a,b)]

c/mol kg^{-1} t/°C	0.80	1.4	3.2	4.6	6.1	7.7	KCl (c=1.0)	KNO_3 (c=4.0)	KNO_2 (c=10.0)
10	48.9	71.5	136	194	252	446	24.6		26.5
15	43.8	64.1	119	174	228	400	22.5		24.4
20	39.5	59.1	105	154	195	343	21.0		22.6
25	36.0	54.1	94.6	141	176	311	19.6		21.3
29	32.1	48.4	83.6	126	161	283	18.1		19.6
34	29.6	43.4	78.3	112	147	260	16.7		18.3
38	27.3	40.4	72.3	103	135	239	15.5	15.3	17.3
43	25.4	37.7	68.0	95.6	121	211	14.6	14.3	16.2
47	24.0	35.9	61.6	91.8	115	198	13.7	13.7	15.6
56	21.8	32.1	55.6	80.5	102	162	12.5	12.4	14.3
66	19.7	29.1	50.6	73.0	91.2	143	11.3	11.5	12.9
ΔE_a(10—34)/kJ mol^{-1}	15	15	17	16	17	17	11	—	11
ΔE_a(38—66)/kJ mol^{-1}	10	10	11	11	13	16	9	9	9

a) All the values were obtained for the isotropic phase even if the liquid crystal phase coexists. b) Standard deviations for all the activation energies were within 1—2 kJ mol^{-1}.

including more than two states, Zimmerman and Brittin expressed the relaxation rate as[6)]

$$R_1 = x_1R_{11} + x_2R_{12} + x_3R_{13} + \cdots, \tag{4}$$

where R_{1i} is the relaxation rate in state i; the mole fraction of component (i) is x_i. The exchange times between the various components are very much shorter than the $T_{1i}(= R_{1i}^{-1})$. In electrolyte solutions, the relaxation rate for the ^{17}O of H_2O can generally be expressed as

$$\begin{aligned} R_1 &= x_CR_{1C} + x_AR_{1A} + x_FR_{1F} \\ &= x_CR_{1C} + x_AR_{1A} + (1 - x_A - x_C)R_{1F}, \end{aligned} \tag{5}$$

where C, A, and F indicate the component of the water of hydration to cations, anions, and free water, respectively. In this equation R_{1i} is larger than R_{1F} for a structure-maker i ion, while it is smaller for a structure-breaker i ion.[7)] In concentrated DBP solutions the very large relaxation rates listed in Tables 1 and 2 show that the aggregation of DBP extensively occurs and that DBP aggregates are strong structure-makers. The free water should therefore be decreased due to hydration to the anion; both of the R_{1C} and R_{1F} values are appreciably smaller than the R_{1A} value in Eq. 5; thus, when comparing the sodium system with the potassium system we can roughly estimate the contribution of hydration for the DBP anion by a correction with the corresponding value for the cation from the results of concentrated simple electrolyte solutions. For this purpose we have also measured the relaxation times for the ^{17}O of H_2O in simple electrolyte solutions, such as sodium nitrate, potassium nitrate, and potassium nitrite solutions. Among them, the solubility of potassium nitrate to water is lower and the highest concentration used for this solution was 4 mol kg^{-1} above 40 °C. The last and second to last columns of Tables 1, 2 list the results for these simple electrolyte solutions. By using some of the data in Tables 1, 2 we can roughly estimate the contribution of the hydration of the DBP aggregates in comparing the sodium and potassium systems. For example, we shall take the relaxation rates of the ^{17}O of H_2O for the 4.6 and 6.1 mol kg^{-1} dibutyl sodium and potassium phosphates at 10, 29, and 66 °C. According to the results for 10 mol kg^{-1} sodium nitrate and potassium nitrite solutions the differences in the contributions of the x_CR_{1C} term between the two cations were 300, 130, and 35 at 10, 29, and 66 °C, respectively. On the other hand, the differences in the relaxation rates between NaDBP and KDP solutions were 770, 240, and 50 for a 4.6 mol kg^{-1} solution, and 1460, 500, 90 for a 6.1 mol kg^{-1} solution at each temperature. Since the relaxation rate is nearly proportional to the concentration in simple electrolyte solutions, the differences in the contribution between the two cations are 140—180, 60—80, and 16—21 at each temperature in the concentration range of 4.6—6.1 mol kg^{-1}. In comparing these values with those for dibutyl phosphate solutions, we can clearly recognize that the hydration of DBP aggregates is appreciably larger in the sodium system than in the potassium one at both 4.6 and 6.1 mol kg^{-1}. Such a comparison between the sodium and potassium systems at lower concentrations also shows that the formation of DBP aggregates occurs more extensively in the sodium system than in the potassium system, even at 0.8 mol kg^{-1}.

Another approach to see the extent of hydration and ion-binding through relaxation data is the temperature dependences of the relaxation rates.[8)] On the right-hand side of Eq. 3, since all of the parameters, except for τ_{eff}, can be considered to be independent of the temperature, the temperature dependency of R_1 is attributed to that of τ_{eff},[9)] which may show an Arrhenius behavior, generally expressed as

$$\tau_{\mathrm{eff}} = A \exp (E_a / RT)$$

or

$$\ln \tau_{\mathrm{eff}} = E_a / RT + \ln A \tag{6}$$

Here, A is a constant and E_a is the activation energy related to the barrier regarding fluctuation of the observed nucleus. Since the rate of relaxation is directly proportional to τ_{eff} (Eq. 3), we can obtain the activation energy for (τ_{eff}) from an Arrhenius plot of R_1. The meaning of the τ_{eff} depends on the kind of the molecule or the ion containing the observed nucleus;[4,7] for the ^{17}O of H_2O it is most clearly defined and is effectively the rotational correlation time of a water molecule; for the ^{23}Na of the sodium ion, which is appreciably hydrated, the translations of water molecules within the first hydration shell mainly contribute to τ_{eff},[4] and for the ^{39}K of the potassium ion, which is very weakly hydrated, both translations and rotations of the water molecules contribute to τ_{eff}, just as being proposed for the chloride ion.[4] We thus used τ_R in the place of τ_{eff} for ^{17}O of H_2O, and τ_{eff} as it is for ^{23}Na and ^{39}K, where the situation is somewhat complicated.

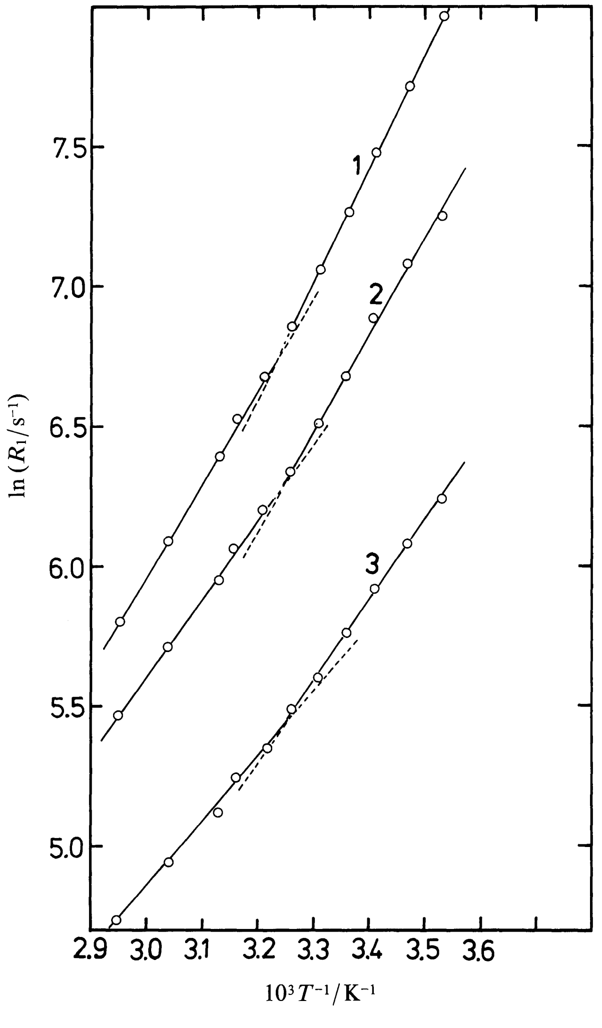

Fig. 2. Typical Arrhenius plots of the relaxation rates for the ^{17}O NMR of water. 1. 6.1 mol kg^{-1} dibutyl sodium phosphate solution. 2. 6.1 mol kg^{-1} dibutyl potassium phosphate solution. 3. 9.6 mol kg^{-1} sodium nitrate solution.

Arrhenius plots of the relaxation rates gave lines which were slightly curved in the range 35—40 °C. Two typical cases for the ^{17}O of water at 6.1 mol kg^{-1} DBPNa and DBPK solutions are depicted in Fig. 2 in comparison with the case of a 10 mol kg^{-1} $NaNO_3$ solution. We thus determined two values of the activation energies, for both τ_{eff} and τ_R: one for the temperature range 10—35 °C and the other for 40—70 °C. All of the results are listed in the bottom rows of Tables 1—4. Since the physical meaning of τ_R for the water is clearer than that of τ_{eff} for alkali ions, we first discuss the result for the τ_R on the basis of the results given in Tables 1, 2. These results show that the activation energies in dibutyl sodium phosphate solutions are 5—8 kJ mol^{-1} larger than those in dibutyl potassium phosphate solutions. These differences can be considered to come from both the alkali ions and the DBP anions. The sodium ion is a structure maker for water, while the potassium ion is a structure breaker; as listed in Tables 1, 2, the activation energies for a concentrated sodium nitrate solution is 6—9 kJ mol^{-1} larger than that for concentrated potassium nitrite and nitrate solutions. This difference between the two cation systems is similar to the difference regarding their hydration.[7] Thus, higher activation energy for NaDBP than that for KDBP can be appreciably attributed to the difference in the hydration between the sodium and potassium ions. From the results concerning the activation energies, therefore, we cannot clearly conclude that the NaDBP aggregates form to a larger extent than do the KDBP ones. This may result from the complicated situation concerning the concentrated and aggregated solutions, i.e., the extent of aggregation may be temperature-dependent; thus, the activation energies obtained for the relaxation rates of the water molecules may not correctly correspond to those for τ_R.

Clear information obtained from the temperature dependences of the ^{17}O relaxation of water molecules is as follows. In DBP solutions the obtained activation energies become larger at higher concentrations, where the DBP aggregates form more extensively; further, the larger activation energies in potassium dibutylphosphate than in simple potassium solutions can be attributed to the higher extent regarding the hydration of DBP aggregates.

The extent of aggregation in a micellar solution is also related to the viscosity. The viscosity (η) of a colloidal system increases with the growth regarding the content of the colloidal phase. This relation is expressed by Einstein's law,

$$\eta = \eta_0(1 + k\phi), \tag{7}$$

where η and η_0 are the viscosities of the colloidal solution and water, respectively, $\phi = V_d / V$ is the volume fraction of the colloidal phase (V_d) in the total volume (V) of the system, and k is a factor determined by the shape of the particles. In comparing similar systems, a more structurized solution has a larger k value and the larger extent of aggregation makes the ϕ value larger. This means that the viscosity is a good indicator to determine the extent of aggregation in colloidal solutions. We, thus, measured the viscosities for both NaDBP and KDBP systems with varying concentrations and temperatures in order to compare the results for NMR relaxation studies.

Tables 5, 6 show the concentration and temperature dependences of η in a NaDBP and KBP solutions. A comparison between the NaDBP and KDBP system for visosity values under any conditions clearly shows that the DBP aggregates form more extensively in a sodium system than in a potassium system, even when considering the contribution of the cations obtained from the results for the corresponding concentrated simple solutions. The activation energies for the viscosities also give information concerning the extent of DBP aggregates. They were obtained from a log(η) vs. $1/T$ plot; the results are listed in the bottom rows in each system. Although the trend is roughly consistent with that seen for the relaxation rates of water molecules (as listed in Tables 1, 2), the activation energies for the viscosities are larger than those for the relaxation rate in both the sodium and potassium systems. Such disagreement between the activation energy for the viscosity and that for the relaxation rate may be due to

Table 5. Concentration and Temperature Dependences of the Viscosity η/mPa s for the Aqueous Sodium Dibutyl Phosphate Solutions Comparing with That for the Concentrated Sodium Nitrate Solutions[b)]

c/mol kg^{-1} t/°C	0.80	1.4	3.2	4.6	6.1	$NaNO_3$ (c=9.6)
10	2.52	4.09	20.2	51.3		3.05
15	2.10	3.43	15.8	38.3		2.64
20	1.79	2.89	13.1	29.6		2.30
25	1.55	2.48	10.7	23.4		2.05
30	1.35	2.15	8.95	18.7	110	1.82
35	1.19	1.89	7.48	15.1	48.8	1.63
40	1.06	1.67	6.32	12.4	24.3	1.47
45	0.959	1.49	5.50	10.3	19.1	1.34
50	0.866	1.33	4.67	8.69	15.6	1.23
60	0.714	1.09	3.55	6.25	11.5	1.05
70	0.611	0.911	2.79	4.93	8.80	0.911
ΔE_a(10—35)/kJ mol^{-1}	22	23	29	36	a)	18
ΔE_a(40—70)/kJ mol^{-1}	17	18	24	28	29	15

a) The Arrhenium plot was largely curved in this temperature range. b) Standard deviations for all the activation energies were within 1 kJ mol^{-1}

Table 6. Concentration and Temperature Dependences of the Viscosity η/mPa s for the Aqueous Potassium Dibutyl Phosphate Solutions[b)]

c/mol kg^{-1} t/°C	0.80	1.4	3.2	4.6	6.1	KNO_3 (c=4)	KNO_2 (c=10)
10	2.38	3.57	13.5	30.0	(85.4)[a)]		1.72
15	2.04	3.00	11.0	24.3	43.9		1.57
20	1.78	2.54	9.14	19.2	32.4		1.45
25	1.62	2.25	7.84	16.2	26.1		1.33
30	1.44	1.97	6.57	12.6	20.8		1.24
35	1.28	1.73	5.70	11.1	17.5		1.15
40	1.14	1.54	4.89	9.35	14.7	0.753	1.08
45	1.01	1.40	4.25	8.03	12.5	0.702	1.01
50	0.933	1.25	3.76	6.92	10.6	0.667	0.950
60	0.794	1.05	2.97	5.31	8.00	0.581	0.847
70	0.670	0.874	2.37	3.99	6.10	0.517	0.771
ΔE_a(10—35)/kJ mol^{-1}	18	21	25	30	35	—	13
ΔE_a(40—70)/kJ mol^{-1}	16	17	21	25	27	12	11

a) This value was omitted for the Arrhenius plot. b) Standard deviations for all the activation energies were within 1 kJ mol^{-1}.

the contrast between the dependence of the viscosity on the extent of aggregations and the dependence of the relaxation rate on the hydration of the DBP aggregates and alkaline ions.

In comparing the sodium and potassium systems, the activation energies of NaDBP solutions are 3—6 kJ mol^{-1} larger than those of KDBP solutions in the high-concentration range; for simple electrolyte solutions, the differences are 3—5 kJ mol^{-1}. When considering the results for the corresponding simple electrolyte solutions, we cannot attribute the difference in the activation energies of the viscosities of the DBP solutions between the two cation systems to the difference in the extent of DBP aggregations. Such an ambiguity regarding the activation energy was also seen in the relaxation time of the water molecules; this may be due to a complicated situation regarding the temperature dependence on the formation of ion aggregates.

Although the definition of the $\tau_{\rm eff}$ value for alkaline ions is somewhat complicated, the concentration dependences of the ^{23}Na relaxation times in a sodium amphiphillic solution provide good information concerning the extent of ion aggregation, such as micelle formation.[10] This method is based on the approach performed by Hertz.[7] According to his approach, the relaxation rates can be expressed as a function of the molality of salt m,

$$R_1 = (R_1)_0(1 + B'm + C'm^2 + \cdots), \qquad (8)$$

where $(R_1)_0$ is the longitudinal relaxation rate for pure water, and B' and C' are constants.[7,11] The B' coefficient can be related to the B coefficient for the viscosity of simple electrolyte solutions, and non-zero C' comes from higher-order interactions of the ions. Fig. 3 shows this relationship for the Na and K DBP systems at both 38 and 66 °C, where all of the solutions are isotropic, as well as for the sodium nitrate system at 66 °C. The plot clearly shows that the ion aggregates form to a great extent from around 4—5 mol kg^{-1} for the NaDBP solution and 6—7 mol kg^{-1} for the KDBP solution. The fact that the change in the slope occurs at a concentration much higher than the critical micelle concentration (about 0.8 mol kg^{-1})[1] for the sodium system shows the presence of higher aggregates than the micelles. This result is consistent with the fact that the activation energies for the relaxation rates increase around 4—5 mol kg^{-1} for the sodium system and 6—7 mol kg^{-1} for the potassium system (Tables 3 and 4), and that aggregation including potassium ions occurred to a smaller extent than that including sodium ions.

As stated above, the correlation times obtained for the sodium and potassium ions are not so clearly defined as those for water molecules. It seems, however, to be significant to compare the activation energies of R_1 for the alkaline ions with those for the water molecules, since the relaxation of the alkali ions is generally dominated by a contribution from water molecules in the first hydration shell. The results listed in the bottom rows of Tables 3, 4 for the sodium and the potassium ions are appreciably smaller than those for the quasi isotropic reorientation (Tables 1, 2) of the water molecules, as well as those for axial reorientation.[2] Since a larger activation energy seems to be necessary for more anisotropic motion, as shown for the ^{1}H and ^{2}H relaxations of water molecules,[2] the activation energies for the sodium $\tau_{\rm eff}$ and the potassium $\tau_{\rm eff}$ are smaller than those for the water molecules, and can be attributed to the contribution of the translational motion of the water molecules to their relaxations, as calculated by Engström et al.[4] With increasing the concentration of DBP the activation energies also gradually increase. Even for simple electrolyte solutions, such as sodium nitrate solutions, as shown in Table 3, the activation energies for the sodium $\tau_{\rm eff}$ are higher at higher concentrations where most of the sodium ions form ion-pairs with the nitrate

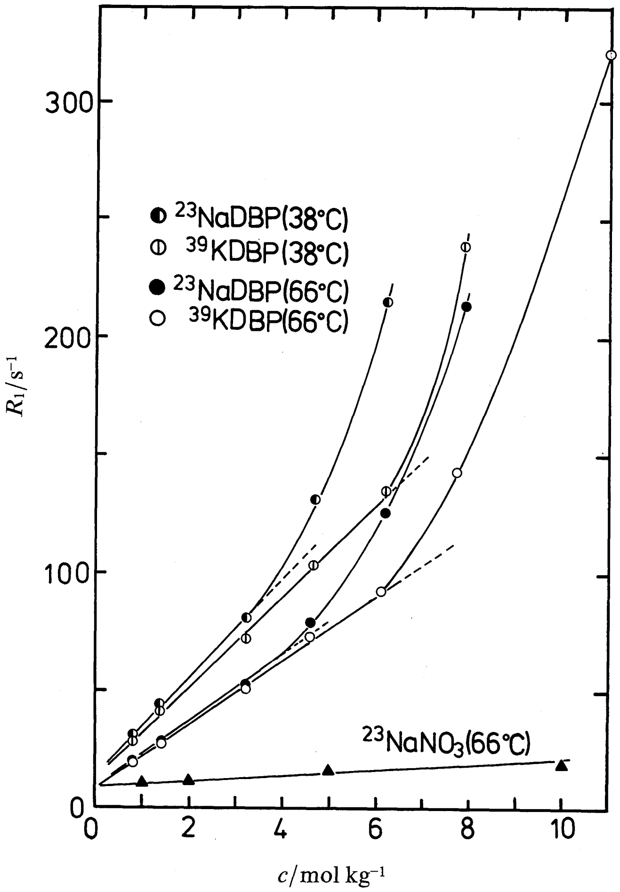

Fig. 3. Dependence of the longitudinal relaxation rates on the DBP concentrations for ^{23}Na of hydrated sodium ion, and for ^{39}K of hydrated potassium ion both at 38 and 66 °C, where all the solutions are isotropic. ^{23}NaNO$_3$: ^{23}Na in the sodium nitrate solution. ^{23}NaDBP: ^{23}Na in the dibutyl sodium phosphate solution. ^{39}KDBP: ^{39}K in the dibutyl potassium phosphate solution.

anions and the values are close to those at high DBP concentrations. Thus, the higher activation energy for the sodium τ_{eff} seems to be attributed to a higher degree of ion-binding to the anions. The results for concentrated potassium nitrite and nitrate solutions, however, indicate that the larger activation energies for the alkali τ_{eff} do not always mean larger ionic interactions with anions, since the potassium ion will more easily form ion-pairs with anions than will the sodium ion. This may also be due to complicated situations concerning ionic interactions in concentrated solutions, even in simple electrolyte solutions.

Through the above considerations, we can see that both the viscosity and the spin-lattice relaxation rates for the water molecules or the alkali ion in the dibutylphosphate solutions showed that the aggregation in the sodium system occurs more extensivly than in the potassium system. Although the activation energies for their relaxation rates also suggest a similar trend, the effect of the cations on the extent of DBP aggregation was not clear when considering the difference in the hydration between the two cations. One reason of this ambiguity comes from the complicated situation, even in simple concentrated electrolyte solutions; for example, the temperature dependences of the extent of ion aggregation will be expected in concentrated and aggregated solution systems. This means that the extent of the hydration and the ion-binding, which are closely related with an extent of the ion aggregations or a size of the ion aggregates, will be significantly changed with a change in the temperatures. With an increase in the extent of formation or in the size of ion aggregates, their temperature dependences will also increase; thus, the activation energies obtained for the relaxation rates and the viscosities of DBP solutions are roughly proportional to the extent of hydration or ion-binding, while they do not correctly correspond to the extent of restriction for the rotational motions (τ_R) of the water molecules or ions.

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