Solution Properties of Dialkyl Phosphate Salts. Apparent Molar Volumes, Viscosity *B* Coefficients, Heats of Solution, and Osmotic Coefficients

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The apparent molar volumes, viscosity *B* coefficients, and heats of solution of sodium salts of dialkyl phosphates (methyl, ethyl, and butyl) in water were measured. The limiting apparent molar volumes at 25 °C increased with the number of carbon atoms in the alkyl chains. The viscosity *B* coefficients of the salts decreased as the temperature was raised from 25 to 35 °C. The changes in heat capacity for dissolution in water, as calculated from the heats of solution at 15, 25, and 35 °C, were positive for the salts. The osmotic coefficients for lithium, sodium, and potassium salts of dimethyl phosphate were also measured. For a given concentration, the osmotic coefficients decreased in the order: $Li^+ < Na^+ < K^+$. From the results obtained, the $-(-O)_2PO_2^-$ ionic part may be classified as a structure-maker.

The physicochemical properties of organic monovalent anions, such as carboxylates and sulfonates in water, have been studied by many investigators.[1-9] Alkali metal salts of dialkyl phosphates ($(RO)_2PO_2M$) are other organic monovalent electrolytes. It seems that it would be interesting to study the properties of aqueous solutions of dialkyl phosphate anions; and the data would help to elucidate the role of the phosphate group in such a biological substance as nucleic acid. In this paper the experimental results will be reported on the apparent molar volumes, viscosity *B* coefficients, and heats of solution of sodium salts of dimethy, diethyl, and dibutyl phosphates in water. In addition, the osmotic coefficients of lithium, sodium, and potassium salts of dimethyl phosphate have also been measured in order to get information on the ion-solvent interaction of the phosphate anion.

Experimental

$(MeO)_2PO_2M$ (M=Li, Na, and K) was prepared by the reaction of trimethyl phosphate with the corresponding alkali metal iodides in acetone.[10] $(EtO)_2PO_2Na$ and $(n\text{-}BuO)_2PO_2Na$ were prepared by the neutralization of the corresponding dialkyl phosphates with a solution of sodium hydroxide, after which the water was evaporated to dryness; the salts were then extracted with ethanol. Commercial diethyl and dibutyl phosphates were purified before hand by the distribution between water and 1-pentanol according to the method of Stewart and Crandall.[11] The salts were purified by recrystallization from suitable solvents: ethanol–water solutions for $(MeO)_2PO_2Li$ and $(MeO)_2PO_2Na$, and ethanol–ethyl acetate solutions for $(MeO)_2PO_2K$, $(EtO)_2PO_2Na$, and $(n\text{-}BuO)_2PO_2Na$. All the salts were hygroscopic; they were dried in vacuo at 60 °C for several days, and the molecular weights were checked by means of volumetric analysis. A known amount of the sample was dissolved in water and passed through an ion-exchange resin in the hydrogen form; the eluent was titrated with a standard NaOH solution. It was found that the obtained samples were anhydrous. Water was triply distilled. The solutions were made by weight.

The densities were measured using a vibrating-tube densimeter, twin-type SS-D-200, of the Shibayama Scientific Co., Ltd. The viscosities were measured at 25 and 35 °C using an automatic viscometer of the Shibayama Scientific Co., Ltd. The details of the procedure were described in a previous paper.[9] The electric conductivities were measured with an LCR meter, AG-4301B, of the Ando Electric Co., Ltd., using a frequency of 1000 Hz.

The heats of solution were measured at 15, 25, and 35 °C using a twin isoperibol calorimeter, TIC-2C, of the Tokyo Riko Co., Ltd., by a method similar to that described in a previous paper.[9]

The osmotic coefficients were measured at 35 °C using a vapor pressure osmometer of Knauer & Co., Ltd. The resistance difference, ΔR, between matched thermistors, one with a drop of the solution, and the other with a drop of the solvent, was measured on a chart recorder 5 min after the application of the solution. At least 5 readings were made on each solution, and the results were averaged. The osmotic coefficents, ϕ, were calculated from the ΔR values using the relation:[12]

$$\phi = \Delta R / K \nu m, \tag{1}$$

where K is the apparatus constant; ν, the total number of ions produced by the complete dissociation of a molecule; and m, the molal concentration. The apparatus was calibrated with NaCl solutions of known molality and osmotic coefficient.[13]

Results and Discussion

Apparent Molar Volumes. The apparent molar volumes, ϕ_v, in $cm^3 mol^{-1}$ were calculated from the densities using the following equation:

$$\phi_v = \frac{1000(\rho_0 - \rho)}{m\rho\rho_0} + \frac{M}{\rho}, \tag{2}$$

where M is the molar mass in $g\ mol^{-1}$ and ρ_0 and ρ are the densities in $g\ cm^{-3}$ of water and of a solution respectively. The apparent molar volume of the electrolytes is given by the equation:[14]

$$\phi_v = \phi_v^\circ + A_v c^{1/2} + B_v c, \tag{3}$$

where ϕ_v° is the limitimg value, which is identical with the partial molar volume at infinite dilution; A_v and B_v are the constants. The value of the constant A_v is 1.868 $cm^3\ dm^{3/2}\ mol^{-3/2}$ for water at 25 °C;[14] the relation $\phi_v - 1.868\,c^{1/2}$ versus c for a series of sodium dialkyl phosphates is shown in Fig. 1. The values of $\phi_v{}^\circ$ and B_v are given in Table 1. It is found that the $\phi_v{}^\circ$ values increase as the alkyl-chain length increases and that the increments in the $\phi_v{}^\circ$ values per methylene group are 14.7 $cm^3\,mol^{-1}$ from dimethyl salt to diethyl salt and 16.1 $cm^3\,mol^{-1}$ from diethyl salt to dibutyl salt. Those results are in accord with Sakurai's opinion[15] that the increments in the $\phi_v{}^\circ$ values per methylene group for homologous organic salts approach about 16 $cm^3\,mol^{-1}$ at 25 °C as the chain length increases. The B_v values are found to decrease with an increase in the number of carbon atoms in the alkyl chains, as is shown in Table 1; this fact is in accord with the results for other homologous compounds.[15,16]

The Viscosity *B* Coefficients. The viscosity of an aqueous solution of an electrolyte, η, for concentrations below 0.1 $mol\,dm^{-3}$ can be represented by the Jones-Dole equation:[17]

$$\eta/\eta_0 = 1 + A_\eta c^{1/2} + B_\eta c, \tag{4}$$

where η_0 is the viscosity of water, and A_η and B_η, the characteristic constants of the solutes. The A_η coefficient was interpreted theoretically by Falkenhagen and Vernon;[18] it can be calculated using the data of the limiting equivalent conductivities of the salt, the cation, and the anion. The B_η coefficient is related to the ion-solvent interaction and to the size and shape of the ion, and it is highly specific for the electrolyte and the temperature. Equation 4 may be converted to:

$$\eta/\eta_0 - 1 - A_\eta c^{1/2} = B_\eta c. \tag{5}$$

When the left-hand side of Eq. 5, using the calculated values of A_η, is plotted against c, the viscosity B coefficient is obtained as the slope of a straight line. Figure 2 shows the results of plotting Eq. 5. The values of A_η and B_η are listed in Table 2.

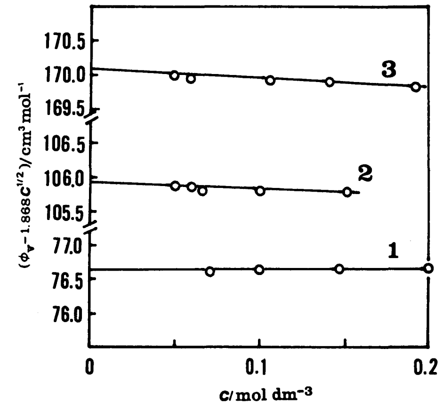

Fig. 1. Apparent molar volumes of $(RO)_2PO_2Na$ at 25 °C. 1: Methyl, 2: ethyl, 3: butyl.

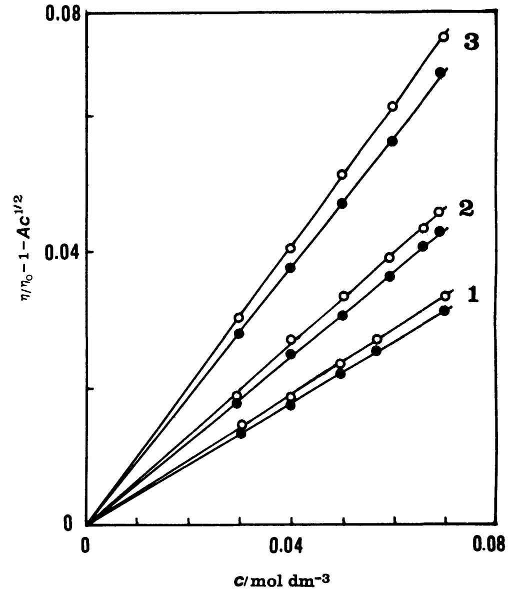

Fig. 2. Plots of $\eta/\eta_0 - 1 - A_\eta c^{1/2}$ against c for $(RO)_2PO_2Na$. 1: Methyl, 2: ethyl, 3: butyl. ○: 25 °C, ●: 35 °C.

Table 1. Limiting Apparent Molar Volume of $(RO)_2PO_2Na$ at 25 °C

$(RO)_2PO_2Na$	$\phi_v{}^\circ/cm^3\,mol^{-1}$	$B_v/dm\,cm^3\,mol^{-2}$
Methyl	76.64	0
Ethyl	105.95	−1.0
Butyl	170.10	−1.5

Table 2. The Values of A_η, B_η, and ΔB of $(RO)_2PO_2Na$

$(RO)_2PO_2Na$	$A_\eta/dm^{3/2}\,mol^{-1/2}$		$B_\eta/dm^3\,mol^{-1}$		$\Delta B/dm^3\,mol^{-1}$
	25 °C	35 °C	25 °C	35 °C	
Methyl	0.0088	0.0089	0.479	0.448	−0.031
Ethyl	0.0094	0.0097	0.667	0.618	−0.049
Butyl	0.0105	0.0106	1.030	0.951	−0.079

The B_η values of homologous sodium dialkyl phosphates are found to increase with the chain length. Figure 3 shows the relationship between the B_η values and the number of carbon atoms in the alkyl chains, n, at 25 °C. The B_η values of sodium alkanoates[4,8] as well as sodium alkanesulfonates[8,9] in the literature are also included in Fig. 3. It is found that the B_η values for the three homologous organic electrolytes with the same number of carbon atoms will be in the order: $(RO)_2PO_2Na > RCOONa > RSO_3Na$. In connection with the viscosities of dialkyl and monoalkyl salts in water, it must be pointed out that the B_η values of dialkylam-

Table 3. Heats of Solution and Heat-Capacity Changes of $(RO)_2PO_2Na$

$(RO)_2PO_2Na$	$-\Delta H_s^\circ$/kJ mol^{-1}			ΔC_p°/JK^{-1}mol^{-1}
	15°C	25°C	35°C	
Methyl	24.52±0.04	24.27±0.04	23.64±0.08	44±7
Ethyl	33.47±0.02	32.01±0.01	30.79±0.03	134±3
Butyl	38.74±0.08	34.77±0.08	30.67±0.04	404±10

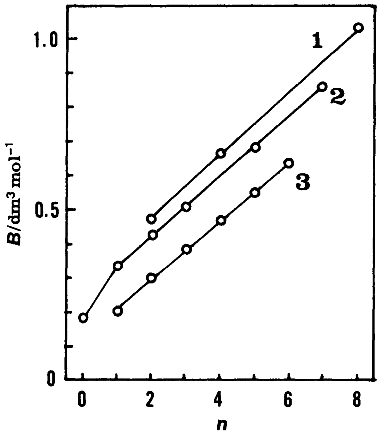

Fig. 3. Plots of viscosity B coefficients for organic salts against number of carbon atoms in the alkyl groups at 25°C.
1: Sodium dialkyl phosphates, 2: sodium alkanoates,[4,8] 3: sodium alkanesulfonates.[8,9]

monium ions are approximately equal to those of monoalkylammonium ions with the same number of carbon atoms.[19]

The temperature dependence of the B_η values may be regarded as an index of the solute-solvent interaction; the B_η values increase with the temperature for a solvent-structure-breaking salt, while they decrease with temperature for a solvent-structure-making solute.[20] For all three compounds used, as may be seen in Table 2, that the B_η values decrease as the temperature is raised from 25 to 35 °C; these salts may therefore be considered to behave as structure-making salts in the water phase. The changes in the viscosity B coefficients which occur as the temperature is raised from 25 to 35 °C, ΔB, are also listed in Table 2. The ΔB values decrease with the number of carbon atoms in the alkyl chains of the series; this means that the hydrophobic hydration increases with the length of the alkyl chains. The B_η values are naturally made up of the sum of the contributions from both sodium and organic ions. Fortunately, the B_η values of the sodium ion are insensitive to the temperature.[21] Therefore, the temperature dependence of the viscosity B coefficients of sodium dialkyl phosphates discussed above conveniently reflects the nature of the dialkyl phosphate ions.

The solvent structural effect may also be evaluated by using the method of Desnoyers and Perron.[22] The B_η value of the ion is interpreted as consisting of two terms; the first is the effect of the ionic size, B_{size}, and the second is the contribution arising from the ion-solvent interaction, B_{solv}. If we assume that the Einstein equation derived for the case of spherical colloid may be applied approximately to the aqueous electrolyte solutions, B_{size} may be obtained by the use of the equation:

$$B_{size} = 0.0025\,\bar{V}^\circ_{ion}, \tag{6}$$

where $\bar{V}^\circ_{ion}$ is the partial molar volume expressed in cm^3 mol^{-1}. Thus, B_{solv} can be derived by the use of the equation:

$$B_{solv} = B_\eta - 0.0025\,\bar{V}^\circ_{ion}. \tag{7}$$

The B_{solv} value can be used as a criterion for determining the structural effect of an ion. A positive value of B_{solv} will correspond to a structure-maker, while a negative value will indicate a structure-breaker. The B_{solv} values at 25 °C for dimethyl, diethyl, and dibutyl phosphate ions, as calculated from the data in Tables 1 and 2, are 0.187, 0.302, and 0.504 dm^{3}mol^{-1} respectively, indicating that the dialkyl phosphate anions studied are all structure-making ions. In this calculation, we adopted the B_η value of sodium ion[21] as 0.084 dm^3 mol^{-1} and the $\bar{V}^\circ_{ion}$ value of sodium ion[23] as −6.6 cm^3 mol^{-1}.

Heats of Solution. Heat-of-solution measurements were carried out in the concentration range of $(0.5-1)\times10^{-3}$ mol dm^{-3}. In this concentration range, any dependence of the heat of solution on the concentration is within the limit of experimental error, so the average of three or more measurements has been taken as the heat of solution at infinite dilution, ΔH_s°. The ΔH_s° values of sodium dialkyl phosphates in water are listed in Table 3. The ΔH_s° values were all exothermic, and the results from the ΔH_s° values were used to calculate the change in the heat capacity for dissolution at infinite dilution, ΔC_p°:

$$\Delta C_p^\circ = \mathrm{d}\Delta H_s^\circ/\mathrm{d}T, \tag{8}$$

where T is the temperature. The ΔC_p° values obtained at 25 °C are also listed in Table 3.

The sign and magnitude of ΔC_p° can be taken as a relative measure of the structural effect upon the solvent water.[24,25] The ΔC_p° values of simple salts indicate negative values, whereas the ΔC_p° values of hydrophobic solutes indicate positive values. As may be seen in Table 3, the sign of ΔC_p° of dimethyl phosphate salt is slightly positive, indicating that dimethyl phosphate salt behaves as a weak structure-maker. The magnitude of ΔC_p° increase with the number of carbon

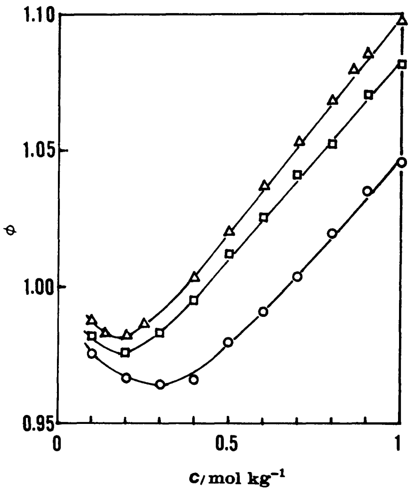

Fig. 4. Plots of osmotic coefficients against molal concentration for $(MeO)_2PO_2M$.
○: Lithium salt, □: sodium salt, △: potassium salt.

atoms in the alkyl chains, and diethyl and dibutyl phosphate salts are excellent structure-makers.

Osmotic Coefficients. Figure 4 indicates the osmotic coefficient versus concentration curves for lithium, sodium, and potassium salts of dimethyl phosphate. It may be seen that for a given concentration the ϕ values decrease in the order: $Li^+ < Na^+ < K^+$. The variation in the order of ion-ion interaction has been discussed by Gurney[26] and by Frank.[27] The rule of Gurney and Frank implied that an anion and a cation with similar structural influences—both being either structure-makers or structure-breakers—will attract each other, whereas if an anion and a cation have different structural tendencies, they will repel each other. Among the cations, Li^+ is a strong, and Na^+, a weak structure-maker, while K^+ is slightly structure-breaking.

As is shown in Fig. 4, the curve for potassium dimethyl phosphate lies at the top, while that for lithium dimethyl phosphate lies at the bottom. Therefore, potassium dimethyl phosphate may be classified as a "breaker-maker" salt, which will give a high-lying osmotic coefficient versus the concentration curve because of the greater escaping tendency between cation and anion. At the opposite extreme, lithium dimethyl phosphate may be classified as a "maker-maker"salt, which will give a lower-lying curve because of the tendency toward more attraction between cation and anion. In this manner, the $-(-O)_2PO_2^-$ ionic part may be classified as a structure-maker.

It must be noted that the acivity coefficients for the alkali metal salts of formic and acetic acids for a given concentration decrease in the order: $Li^+ < N^+ < K^+$.[28] By the application of the rule of Gurney and Frank to this results, formate and acetate ions may be classified as structure-makers. Recently, Miyajima, Sawada, and Nakagaki[4] reported that formate ion is neither a structure-maker nor a structure-breaker, because the viscosity B coefficients of formate ion were practically constant between 15 and 35 °C. However, in view of the sequence of activity coefficients for alkali metal salts of formic acid, formate ion may be considered still to behave as a weak structre-making ion, and it seems that the solvent structural effect of formate ion need to be investigated further.

In addition, the activity coefficients for the salts of *p*-toluenesulfonic acid[29] as well as those for the salts of methane- and ethanesulfonic acid[5] in dilute solutions increase in the order: $Li^+ > Na^+ > K^+$. The application of the rule of Gurney and Frank to these results indicate that these sulfonate ions may be classified as structure-breaking ions. The structure-breaking properties of sulfonate anions have been discussed by Uedaira and Uedaira[6] on the basis of their electric conductivities, and by Katayama et al.[7] on the basis of their partial molar volumes.

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