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NMR Studies on Molecular Interactions Involved in Alkali Metal Halide–Amide–Glycol Ternary Systems

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Interactions in a ternary solution of alkali metal halide–amide–glycol have been investigated on the basis of NMR measurement of chemical shifts of OH proton of glycol and amidic protons of acetamide. Measurements were carried out with various alkali metal halides (MX, M=Li, Na, K, X=Cl, Br, I) and glycols (mono-, di-, tri-, and tetraethylene glycol). The dependency of the chemical shifts on solute concentration was examined with a ternary solution of potassium iodide–acetamide–ethylene glycol. The addition of alkali metal halide to respective glycols or glycolic solutions of acetamide gave rise to a change in chemical shift values. The observed changes were related to the ionic sizes of cations and anions of alkali metal halides and to the number of oxyethylene units in a glycol molecule. It was found that a large ion induces a higher magnetic field shift of resonance positions of glycolic OH proton and amidic proton at trans position than a small ion, the magnitude of the shift change being almost proportional to the concentration of ion, and halogen anion formed in glycolic solution tending to interact with hydrogen at trans position rather than at cis position. From a comparison with the values for chemical shifts of water proton in aqueous alkali metal halide solution, it is suggested that the contribution of alkali metal halide to the chemical shift changes in glycolic solution is similar to those in aqueous solution.

Some aliphatic amides interact with various inorganic salts to form stable complexes. Investigations have been made on their isolation,[1] X-ray analysis,[2,3] electric conductivity,[4–7] heat of solution,[8–14] and infrared spectra.[15] In the preceeding paper,[16] we reported that a similar interaction takes place also in gas-chromatographic stationary phase and is applicable to the specific separation of amides. The interaction between acetamide and lithium iodide in polyethylene glycol (PEG) is as strong as −2.5 kcal/mol of partial molar free energy of transfer from PEG to LiI-containing PEG, which is large enough to attain specific retardation of acetamide elution. It is difficult, however, to consider the structural aspects of the interaction from gas-chromatographic findings.

NMR spectroscopy has been extensively used for the study of aqueous electrolyte and non-electrolyte solutions. Shoolery and Alder[17] discussed the chemical shift of water proton in aqueous diamagnetic salt solution. Fabricand and Goldberg[18] investigated the relationship between proton resonance position and the ionic charge, radius, and concentration of alkali metal halide in aqueous solution, and Hinton and Ladner[19] the structure of a series of amides in aqueous solution. Sunners *et al.*[20] found the non-equivalence of two amide protons of formamide owing to the energy barrier hindering C–N bond rotation. The non-equivalence of two amide protons was also observed when the bromide ion was added to acetonitrile solution of formamide.[21] Hindman[22] studied the effect of the change in concentrations of salts of diamagnetic ions on the chemical shift of water proton. It is known from NMR measurements of ethylene proton of polyethylene glycol (PEG) that PEG associates with potassium iodide in methanol solution to behave as a polyelectrolyte. This phenomenon has been ascribed to ion-dipole interaction between potassium cation[23,24] (or, iodide anion[25]) and etherate oxygen of PEG. No paper seems to have described NMR studies on glycol solution of acetamide and/or alkali metal halide.

In connection with our gas-chromatographic studies on alkali metal halide–amide interaction in PEG stationary phase, we have attempted to consider the interaction from the NMR data of the ternary solution and to compare the results with those obtained in aqueous solution.

Experimental

A Varian A-60 NMR spectrometer operating at 60 MHz and 33.7±1.0 °C was used. Since the chemical shift of glycolic methylene proton determined by use of TMS as an internal standard is independent of addition of alkali metal halide and acetamide, it was used as a standard signal for the chemical shifts of glycolic OH proton and amidic protons.

Ethylene glycol(EG) and triethylene glycol(triEG)(Wako Pure Chemical Industry, Osaka, Japan), diethylene glycol (diEG)(Nakarai Chemicals, Kyoto, Japan), and tetraethylene glycol(tetraEG) (Tokyo Kasei Kogyo, Tokyo, Japan) were dried with sodium metal or anhydrous sodium sulfate and purified by double distillation under a reduced pressure with dry nitrogen gas bubbiling. The gas-chromatographic analysis of the distilled glycols on Tenax GC column indicated no impurity peaks within the full scale recorder response of the main peak. The purity of acetamide(AA) (Wako Pure Chemical Industry) was also checked by GC using PEG 20 M column, showing a single clear peak. Alkali metal halides of reagent grade were completely dried over phosphorus pentoxide before use.

Results

The chemical shift change, $\Delta\sigma(-\Delta\delta)$, was calculated by

$$\Delta\sigma = -(\delta-\delta_0), \tag{1}$$

where δ and δ_0 are the chemical shifts(ppm) of protons in sample solution and in reference solution, respectively. Pure glycol and a solution of AA/glycol=1/9 by mole ratio were used as a reference for the measurements of the chemical shift changes of glycolic OH proton($\Delta\sigma_{OH}$) and of trans and cis (geometrical position to amide oxygen) amide protons ($\Delta\sigma_{NH,t}$, $\Delta\sigma_{NH,c}$),

Table 1. Chemical shifts and shift changes of glycolic OH proton and *trans* and *cis* amide protons with varying concentrations of KI and AA in ethylene glycol

m_{KI}	m_{AA}	X_{KI}	X_{AA}	δ_{OH}	$\delta_{NH,c}$	$\delta_{NH,t}$	$\Delta\sigma_{OH}$	$\Delta\sigma_{NH,c}$	$\Delta\sigma_{NH,t}$
0.00	0.00	0.000	0.000	5.20	—	—	0.00	—	—
0.41	0.00	0.025	0.000	5.07	—	—	0.13	—	—
0.00	0.41	0.000	0.025	5.20	6.92	7.59	0.00	0.02	0.00
0.85	0.00	0.050	0.000	4.94	—	—	0.26	—	—
0.42	0.42	0.025	0.025	5.07	6.89	7.55	0.13	0.05	0.04
0.00	0.85	0.000	0.050	5.19	6.94	7.58	0.01	0.00	0.01
1.79	0.00	0.100	0.000	4.68	—	—	0.52	—	—
1.34	0.45	0.075	0.025	4.82	6.82	7.48	0.38	0.12	0.11
0.90	0.90	0.050	0.050	4.94	6.88	7.51	0.26	0.06	0.08
0.45	1.34	0.025	0.075	5.07	6.91	7.57	0.13	0.03	0.02
0.00	1.79	0.000	0.100	5.20	6.94	7.59	0.00	0.00	0.00
2.84	0.00	0.150	0.000	4.45	—	—	0.75	—	—
2.13	0.71	0.113	0.038	4.63	6.77	7.37	0.57	0.17	0.22
1.42	1.42	0.075	0.075	4.82	6.81	7.44	0.38	0.13	0.15
0.71	2.13	0.038	0.113	5.01	6.87	7.51	0.19	0.07	0.08
0.00	2.84	0.000	0.150	5.19	6.94	7.58	0.01	0.00	0.01
4.03	0.00	0.200	0.000			insoluble			
3.02	1.01	0.150	0.050	4.44	6.72	7.29	0.76	0.22	0.30
2.01	2.01	0.100	0.100	4.69	6.79	7.40	0.51	0.15	0.19
1.01	3.02	0.050	0.150	4.94	6.88	7.49	0.26	0.06	0.10
0.00	4.03	0.000	0.200	5.18	6.94	7.57	0.02	0.00	0.02

m; molality(mol/kg EG), *X*; mole fraction, δ; chemical shift(ppm), $\Delta\sigma$; chemical shift change(ppm, defined by Eq. 1).

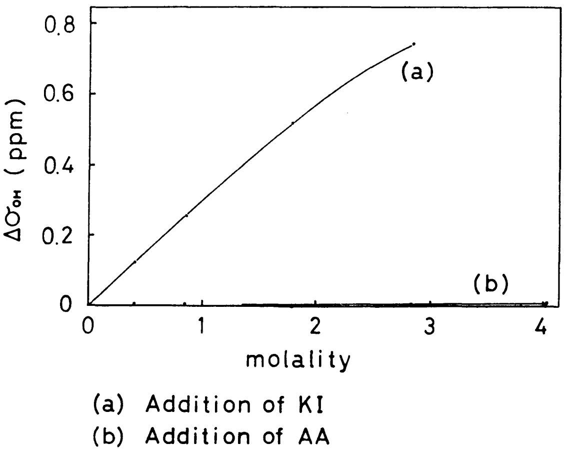

Fig. 1. Relationship between chemical shift change of glycolic OH proton and molality of KI or acetamide in ethylene glycol solution.

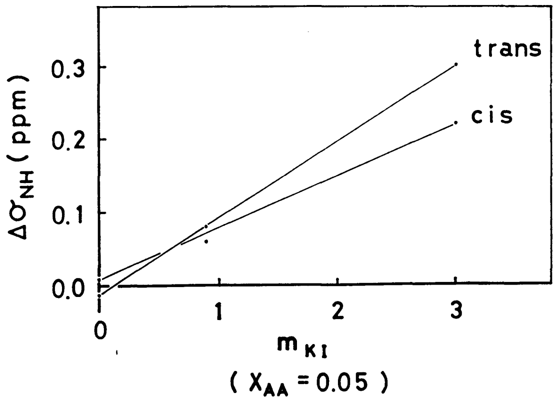

Fig. 2. Relationship between chemical shift changes of trans and cis amide protons and molality of KI at a fixed mole fraction of acetamide (X_{AA}=0.05) in ethylene glycol solution.

respectively. The results obtained in KI–EG and AA–EG binary solutions and in KI–AA–EG ternary solution, where mole fractions of KI(X_{KI}) and AA(X_{AA}) are varied from 0 to 0.2 and from 0 to 0.15, respectively, are given in Table 1. The addition of KI to EG (Fig. 1) gave rise to a high field shift of glycolic OH proton resonance position ($\Delta\sigma_{OH}>0$) proportional to the increase in its molality, whereas the addition of AA had little effect on $\Delta\sigma_{OH}$. In an aqueous solution, a linear relationship between salt concentration and $\Delta\sigma_{OH}$ of water proton was found by Fabricand and Goldberg,[18] the relationship deviating from the linearity in relatively high salt concentration range. The deviation was attributed to the shielding effect of more than one ions on a water proton. Such an effect was not clearly observed in the present case. The interstitial effect,[19] which leads to low field shift of water proton resonance position in dilute aqueous amide solution indicating the stabilization of water structure, was not observed in EG solution. The results for chemical shifts and shift changes of trans and cis amide protons with change in the concentration of KI, are also given in Table 1. It was found that two amide protons of AA give distinct resonance positions ($\delta_{NH,t}>\delta_{NH,c}$), suggesting their non-equivalence. The relationship between $\Delta\sigma_{NH,t}$ or $\Delta\sigma_{NH,c}$ and molality of KI (m_{KI}) is shown in Fig. 2 where X_{AA} is fixed at 0.05. The increasing molality of KI produces almost linear increase in both $\Delta\sigma_{NH,t}$ and

Table 2. The optimum coefficients for the equation, $\Delta\sigma = A\cdot m_{\mathrm{KI}} + B\cdot m_{\mathrm{AA}} + C$

$\Delta\sigma$		A	B	C	r_{KI}[a)]	r_{AA}[a)]	n[b)]
$\Delta\sigma_{\mathrm{OH}}$	EG	0.26	−0.01	0.02	0.998	−0.381	20
	diEG	0.29	−0.03	0.00	0.999	−0.893	19
	triEG	0.17	−0.08	−0.01	0.989	−0.953	19
	tetraEG	0.14	−0.10	−0.01	0.961	−0.928	21
$\Delta\sigma_{\mathrm{NH,t}}$	EG	0.10	0.01	−0.01	0.994	0.534	15
	diEG	0.06	0.00	−0.01	0.954	−0.263	14
	triEG	0.01	−0.01	0.01	0.339	−0.317	14
	tetraEG	−0.05	−0.05	0.02	−0.755	−0.755	16
$\Delta\sigma_{\mathrm{NH,c}}$	EG	0.07	−0.01	0.02	0.987	−0.483	15
	diEG	0.05	−0.03	0.02	0.961	−0.882	14
	triEG	0.04	−0.03	0.03	0.851	−0.807	14
	tetraEG	0.05	−0.07	0.04	0.729	−0.877	16

a) Partial correlation coefficient. b) Number of trials.

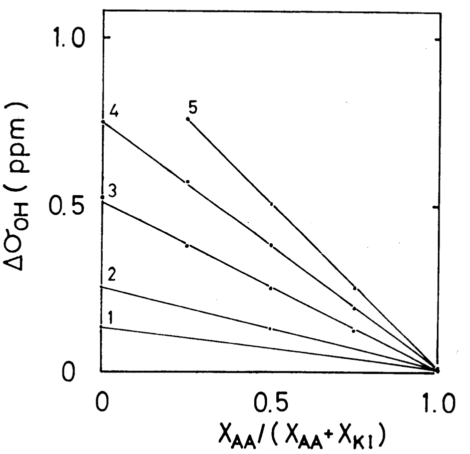

Fig. 3. Relationship between chemical shift change of glycolic OH proton and mole fraction of acetamide with varying total mole fraction of KI and acetamide in ethylene glycol solution (1; $X_{\mathrm{KI}}+X_{\mathrm{AA}}=0.025$, 2; 0.05, 3; 0.1, 4; 0.15, and 5; 0.2).

$\Delta\sigma_{\mathrm{NH,c}}$, the magnitude of increase in $\Delta\sigma_{\mathrm{NH,t}}$ being larger than that in $\Delta\sigma_{\mathrm{NH,c}}$.

Linear relationship also holds between $\Delta\sigma_{\mathrm{OH}}$ and mole fraction of KI (or AA) with change in total mole fraction of KI and AA in KI–AA–EG ternary solution (Fig. 3). This suggests that the contribution of KI and AA to $\Delta\sigma_{\mathrm{OH}}$ can be expressed by a linear combination of respective molalities in the form

$$\Delta\sigma_{\mathrm{OH}} = A\, m_{\mathrm{KI}} + B\, m_{\mathrm{AA}} + C, \tag{2}$$

where the coefficients A and B represent the degree of contribution and C is the intercept. The optimum values for the coefficients were estimated by means of the least squares method using the data given in Table 1. The resulting equation is given in Table 2 along with those for $\Delta\sigma_{\mathrm{NH}}$ in the same solution. The value for A coefficient (0.26) is almost equal to the slope of the line(a) in Fig. 1 and is far larger than coefficient B. This means that KI exerts a predominant effect on $\Delta\sigma_{\mathrm{OH}}$ and the contribution of AA is as small as that of the intercept which should essentially be zero. With $\Delta\sigma_{\mathrm{NH}}$, the trans amide proton seems to be more affected by the addition of KI than the cis proton.

$\Delta\sigma_{\mathrm{OH}}$ values for four glycols added with various alkali metal halides at a mole ratio of MX/glycol=1/9 are given in Table 3. The addition of alkali metal halide except lithium chloride to EG produces high field shift of glycolic OH proton. A certain relationship seems to hold between the magnitude of the shift change and the ionic size. Thus, on the assumption that the surface charge of ion is involved in the electrostatic interaction, the squared reciprocals of ionic radii (r_c^{-2}) of anions and cations of alkali metal halides added are plotted against $\Delta\sigma_{\mathrm{OH}}$ in EG solution (Fig. 4). It was found that the increasing r_c^{-2} of halogen anion having a cation in common is proportional to the decrease in $\Delta\sigma_{\mathrm{OH}}$. The relationship between $\Delta\sigma_{\mathrm{OH}}$ and cationic size indicates that the larger cation causes the more positive shift change in resonance position of glycolic OH proton (Fig. 4). However, the effect, as a whole, is smaller than that of anions; the size effect of anion on $\Delta\sigma_{\mathrm{OH}}$ is greater than that of cation. It is of interest to compare such behavior of ions in glycolic solution with that in aqueous solution. The contribution of individual ion to $\Delta\sigma_{\mathrm{OH}}$ of water proton in aqueous alkali metal halide solution is shown in Fig. 5. A strong resemblance is found between Figs.

Table 3. Chemical shift change of glycolic OH proton of mono-, di-, tri-, and tetraethylene glycol in the presence of various alkali metal halides at mole ratio of MX/glycol=1/9

Salt	$\Delta\sigma_{\mathrm{OH}}$(ppm)			
	EG	diEG	triEG	tetraEG
LiCl	−0.02	−0.15[a)]	−0.24	−0.26
LiBr	0.10	−0.02	−0.14	−0.16
LiI	0.26	0.08	−0.08	−0.08
NaCl	0.19[a)]	0.04[a)]	−0.16[a)]	−0.17[a)]
NaBr	0.34	0.13	−0.04[a)]	−0.04[a)]
NaI	0.47	0.26	0.09	0.05
KCl	0.20[b)]	0.13[b)]	−0.09[a)]	−0.14[a)]
KBr	0.37[a)]	0.17[a)]	0.01[a)]	−0.02
KI	0.52	0.30	0.13	0.07

a) Calculated from twice the $\Delta\sigma_{\mathrm{OH}}$ value obtained from a solution of MX/glycol=1/19 by mole ratio. b) Calculated from four times the $\Delta\sigma_{\mathrm{OH}}$ value obtained from a solution of MX/glycol=1/39 by mole ratio.

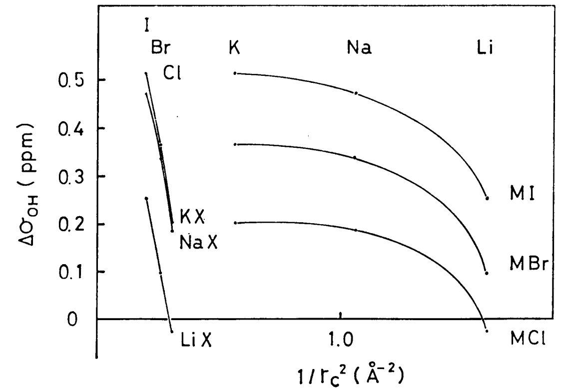

Fig. 4. Ionic size effect on the chemical shift change of glycolic OH proton in a solution of MX/EG=1/9 by mole ratio.

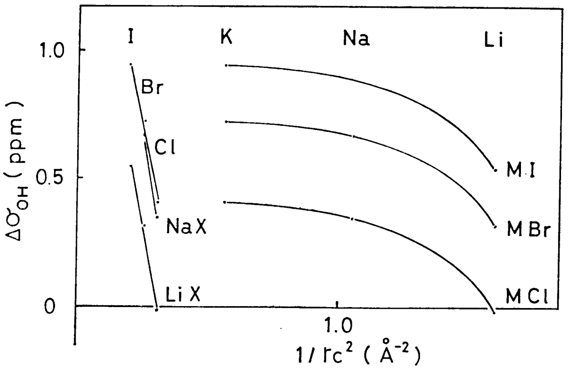

Fig. 5. Ionic size effect on the chemical shift change of water proton in a solution of MX/H_2O=1/9 by mole ratio. The data were obtained from Ref. 18 and corrected with respect to salt susceptibilities[26] according to Wiedeman law.

4 and 5.

Figure 6 shows the relationship between $\Delta\sigma_{OH}$ measured in a solution of MX/AA/EG=1/1/18 by mole ratio and the ionic sizes of alkali metal halides. As compared with Fig. 4 where mole ratio is MX/EG=1/9, Fig. 6 indicates that the general profile of $\Delta\sigma_{OH}$ remains unchanged against the variation of molality of each component, whereas the magnitude of the shift change is about half of those in Fig. 4. This suggests the additive property of $\Delta\sigma_{OH}$ with respect to the concentration of alkali metal halide in relatively low concentration region, since AA has little contribution to $\Delta\sigma_{OH}$. Figure 7 shows the cases of $\Delta_{NH,t}$ and $\Delta\sigma_{NH,c}$; $\Delta\sigma_{NH,t}$ is obviously more dependent on the ionic sizes of alkali metal halides especially on anionic size than $\Delta\sigma_{NH,c}$, although both magnitudes are smaller than that of $\Delta\sigma_{OH}$.

The contribution of individual ions to the change in $\Delta\sigma$ values was evaluated by means of analysis of variance using the data given in Figs. 6 and 7. The presumed values for $\Delta\sigma_{OH}$ and $\Delta\sigma_{NH,t}$ given as a sum of respective ions are in agreement with the observed values. The variance ratios for $\Delta\sigma_{OH}$ and $\Delta\sigma_{NH,t}$ among cations and anions are larger than the value for a level of significance at 5% ($F^1_4(0.05)=6.94$), but the variance ratio of $\Delta\sigma_{NH,c}$ is too small to recognize significant difference. The results seem to support the idea of ionic dissociation of alkali metal halide in glycolic solution.

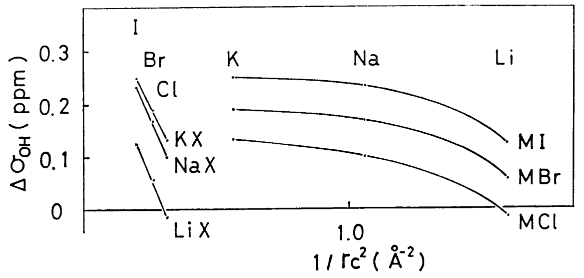

Fig. 6. Ionic size effect on the chemical shift change of glycolic OH proton in a solution of MX/AA/EG=1/1/18 by mole ratio.

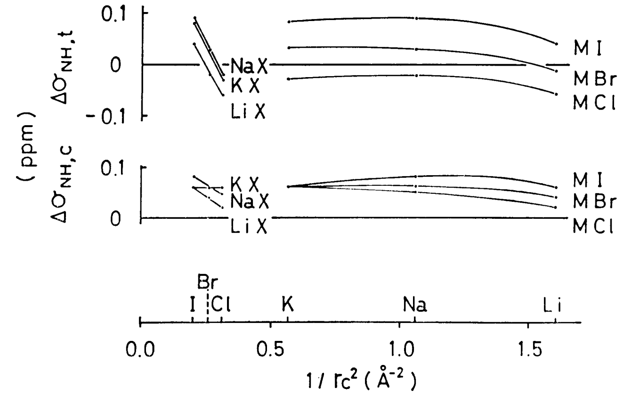

Fig. 7. Ionic size effect on the chemical shift change of amide protons in a solution of MX/AA/EG=1/1/18 by mole ratio.

Experiments were also carried out for higher glycolic solutions (di-, tri-, and tetraEG). It was observed that the increase in the number of oxyethylene units in a glycol molecule is accompanied by a high field shift of OH proton resonance position of pure glycol (EG; δ=5.20, diEG; δ=4.95, triEG; δ=4.50, and tetraEG; δ=4.31). Figure 8 gives the plots of chemical shifts (δ) of glycolic OH and amide protons *vs.* mole fraction of AA (or KI) ($X_{AA}+X_{KI}=0.1$) in di, tri, and tetraEG solutions, showing the linear relationships between δ and X_{AA} (or X_{KI}) in each glycolic solution. It was found that the increase in the oxyethylene unit number is accompanied by high field shifts (decrease in δ value) of all the proton resonance positions, with which the slope, δ/X_{AA}, becomes small. As for the amide protons, the resonance positions are less dependent on the variation in X_{AA} (or X_{KI}) than that of glycolic OH proton.

The chemical shift changes ($\Delta\sigma_{OH}$, $\Delta\sigma_{NH,t}$, and $\Delta\sigma_{NH,c}$) in di-, tri-, and tetraEG solutions are expressed as functions of m_{KI} and m_{AA} as in Eq. 2 according to the method of least squares. The resulting equations, given in Table 2, indicate that $\Delta\sigma_{OH}$ receives a positive contribution($A>0$) from m_{KI} in all the glycolic solutions and a negative contribution($B<0$) from m_{AA} in di-, tri-, and tetraEG solutions. With amide protons, the A coefficient for $\Delta\sigma_{NH,t}$ decreases with increase in the number of oxyethylene units, becoming

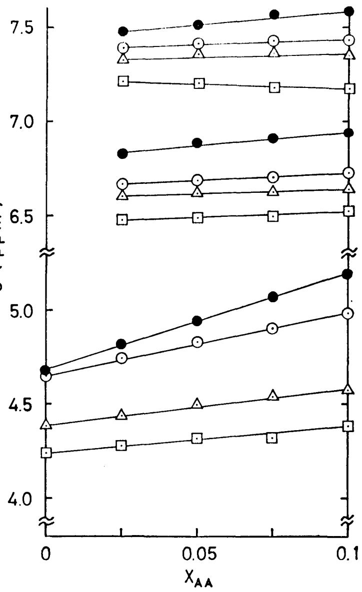

Fig. 8. Relationship between chemical shifts of glycolic OH and amide protons and mole fraction of KI (or AA) with varying oxyethylene unit number in glycol molecule. ($X_{AA}+X_{KI}=0.1$) ●; EG, ⊙; diEG, △; triEG, and ⊡; tetraEG.

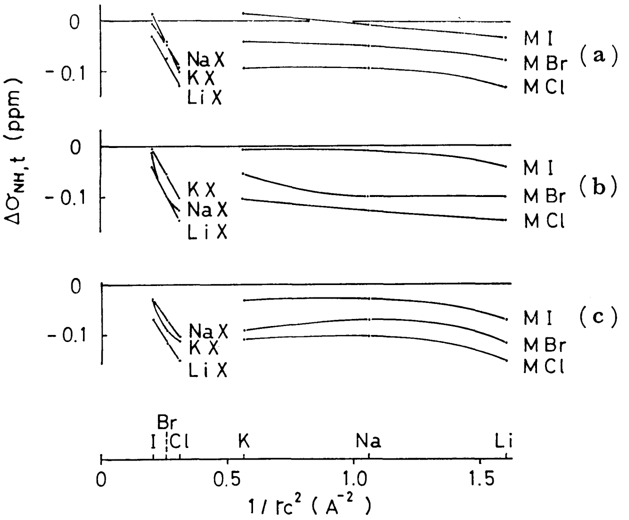

Fig. 9. Ionic size effect on the chemical shift change of trans amide proton in a solution of MX/AA/glycol=1/1/18 by mole ratio (a; diEG, b; triEG, c; tetraEG).

negative in tetraEG solution. No such explicit change is observed in $\Delta\sigma_{NH,c}$.

The change in OH proton resonance positions of mono to tetraEG (*i.e.*, $\Delta\sigma_{OH}$) decreases with the increase in the number of oxyethylene unit in a glycol molecule with different rate among alkali metal halides added (Table 3). The tendency is almost unchanged irrespective of the addition of AA to alkali metal halide–glycol binary system. In a ternary solution consisting of MX/AA/glycol=1/1/18 by mole ratio, the variation in alkali metal halide causes a more significant difference in $\Delta\sigma_{OH}$ and $\Delta\sigma_{NH,t}$ values than in $\Delta\sigma_{NH,c}$ values in each glycol solution. This suggests that the contribution of alkali metal halide to $\Delta\sigma_{OH}$ and $\Delta\sigma_{NH,t}$ may be delivered to the individual ions. The results thus obtained by means of analysis of variance prove that the larger the anionic size, the larger the $\Delta\sigma$ values. The general profile of ionic size effect on $\Delta\sigma_{OH}$ in di-, tri-, and tetraEG solutions are similar to those in EG solution (Fig. 6). However, the magnitude of $\Delta\sigma_{OH}$ decreases with the increase in the oxyethylene unit number. A similar trend was observed in the relationship between ionic size and $\Delta\sigma_{NH,t}$ in di-, tri-, and tetraEG solutions. The difference in molecular weight of glycol produces almost no change in the ionic size effect on $\Delta\sigma_{NH,t}$ (Fig. 9). In all the glycolic solutions, the increase in anionic size gives rise to more increase in $\Delta\sigma_{NH,t}$ than in $\Delta\sigma_{NH,c}$. The $\Delta\sigma_{NH,t}$ value, however, is negative in higher glycolic solutions.

Discussion

Let us first consider the effects which might cause the change in the resonance position of glycolic OH proton. If acetamide is added to glycol, it may affect the hydrogen bondings of glycol. Since acetamide is a non-electrolyte, glycolic OH proton resonance position may be dominated by the change in the hydrogen bondings. Thus, it is assumed that a high field shift of OH proton resonance position ($\Delta\sigma_{OH}>0$) indicates a decrease in hydrogen bondings in the system. The results (Table 1 and Fig. 1) in which little increase in $\Delta\sigma_{OH}$ accompanies the addition of acetamide to ethylene glycol over the concentration range examined, suggest that the AA–EG hydrogen bond may be as strong as the EG–EG hydrogen bond. The addition of alakli metal halide to glycol, on the other hand, produces a different situation, since dissolution of alkali metal halide in glycol is accompanied by ionic dissociation. Approaching glycol molecule, the ions can interact with dipole of glycol molecule, inducing polarization of OH group, decreasing electronic shielding of OH proton to result in an apparent low field shift of OH resonance position. Thus, the observed value for the chemical shift (δ_{OH}) can be expressed as a function of the electrostatic interaction in addition to the effect on hydrogen bondings. A similar but more detailed consideration has been made with respect to water proton resonance position in aqueous electrolyte solution, the salt-effect on water structure being discussed.[22] Some physico-chemical properties of glycol (*i.e.* heat of vaporization, boiling point, and viscosity)[27] suggest that glycol as well as water may have a certain structure due to hydrogen bondings, although there is no explicit evidence. In this connection, it is interesting to note that the strong resemblance found between Figs. 4 and 5 may give a clue for understanding the behavior of ion in glycol solution.

A linear increase in $\Delta\sigma_{OH}$ with increasing KI concentration (Fig. 1) suggests that EG–EG hydrogen bondings may be decreased by the addition of KI. The results given in Table 3 and Fig. 4 indicate that, as compared with a large anion, a small anion (with large surface charge) induces more decrease in the electronic shielding of glycolic OH proton to give a smaller $\Delta\sigma_{OH}$ value.

Amidic protons at the trans and cis positions of acetamide are also involved in hydrogen bonding with glycol molecule. The addition of alkali metal halide, therefore, may have an influence on amide protons as well. The results shown in Figs. 2 and 7 may be interpreted as follows: When alkali metal halide is dissolved in an EG solution of acetamide, the ions formed give rise to apparent decrease in hydrogen bondings of amidic protons to result in high field shifts ($\Delta\sigma_{NH}>0$), halogen anion tending to interact with amide at trans position rather than at cis position.

From the results in Tables 2 and 3 and Fig. 8, it seems that the increase in the number of oxyethylene units in a glycol molecule is accompanied by enhancement of electrostatic interaction of alkali metal halide with acetamide. Such effect may be responsible for the specific retention of amide on an alkali metal halide-containing PEG as a gas-chromatographic stationary phase.

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