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The Viscosity and Conductivity of Aqueous Solutions of Electrolytes Mixed with Glycine and Urea

By Tokuzo TONOMURA and Katsunobu OKAMOTO

Department of Chemistry, Faculty of Science, Kanazawa University, Kanazawa

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The viscosities, the densities, and the conductivities of aqueous solutions of electrolytes mixed with glycine or with urea have been measured at 15, 25 and 35°C. The relative viscosities and the relative conductivities of the mixed solutions have been expressed by the empirical formulae, $\eta=\eta'+\eta_0\beta C$ and $\varLambda=\varLambda_0(1-\gamma C)$, respectively. The retarding effect of glycine on the conductivity of the strong electrolytes has been found to be greater than that of urea in the mixed solutions. The states of the hydration of glycine, urea and the strong electrolytes have been discussed on the basis of the relations between B-values in the viscosity formula of Jones and Dole and the effective volumes in aqueous solutions.

Some studies of the electrochemical properties of aqueous solutions of strong electrolytes using several methods have been reported,[1-4] but only a few data are available in the literature[5-8] for aqueous solutions of mixed electrolytes. The purpose of the present study is to obtain some information concerning hydration and related problems, and to determine the behavior of weak electrolytes from measurements of the viscosity, density and conductivity of various electrolyte solutions in which weak electrolytes are mixed with strong electrolytes. In the present studies, glycine and urea[9] were used as weak electrolytes, and potassium chloride and lithium chloride, as strong ones. An aqueous solution of potassium chloride has a negative viscosity coefficient, while that of lithium chloride is well known to have an abnormal concentration dependence of the viscosity. The viscosity coefficients and densities of aqueous solutions of electrolytes were measured over and appropriate concentration range. Their conductivities were also measured in order to compare the retarding effects of glycine on the mobility of ions with those of urea. The viscosity formula of Jones and Dole is:

$$\eta = \eta_0(1 + AC^{1/2} + BC) \tag{12}$$

where η is the viscosity of the solution; η_0, that of the medium, and C, the concentration of the solute, A and B being constants characteristic of the solute. The A coefficient in the above formula is considered to be chiefly due to the contribution of interionic forces, electrostatic in nature, and the B coefficient to the interaction between solute and solvent in the solution. As the second term, AC, in Eq. 1 is usually so small that it can be neglected,[10] Eq. 1 becomes:

$$\eta = \eta_0(1 + BC) \tag{2}$$

According to Stokes and Mills,[11] the B coefficient in Eq. 2 may be expressed as follows:

$$\eta^{\mathrm{E}} + \eta^{\mathrm{A}} + \eta^{\mathrm{D}} = \eta_0 BC \tag{3}$$

where η^{E} is the viscosity increment arising from the size and shape of an ion; it normally increases with an increase in the ion size. η^{A} is the increment due to the alignment or orientation of polar molecules by the ionic field. η^{D} is the viscosity change associated with the distortion of the solvent structure; this effect can be interpreted as being due to competing forces from the solvent structure in the bulk and from the ionic field. It will cause the viscosity to decrease.

One gram of solution, whose specific volume is v at concentration of C mol./l., contains x g. of solute of the molecular weight M and $(1-x)$g. of solvent. Then,

$$x = MC/1000\rho \tag{4}$$

where ρ is the density of the solution. We assume that the partial specific volume of the solute in

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[1] H. S. Harnd and B. B. Owen, "Physical Chemistry of Electrolytic Solutions," Reinhold Publ. Corp., 3rd. Ed., New York (1957).

[2] R. W. Gurney, "Ionic Processes in Solution", McGraw-Hill Book Co., New York (1953).

[3] M. Kaminsky, *Discussions Faraday Soc.*, **24**, 171 (1957).

[4] E. R. Nightingale, Jr., *J. Phys. Chem.*, **63**, 1381 (1959).

[5] R. M. Roberts and J. G. Kirkwood, *J. Am. Chem. Soc.*, **63**, 1373 (1941).

[6] E. J. King, ibid., **73**, 155 (1951).

[7] J. M. Stokes and R. H. Stokes, *J. Phys. Chem.*, **60**, 217 (1956).

[8] R. A. Robinson and R. H. Stokes, "Electrolyte Solutions," Butterworths Scientific Publ., London (1955).

[9] V. K. Venkatesan and C. V. Suryanarayana, *J. Phys. Chem.*, **60**, 775 (1956).

[10] R. H. Stokes and R. Mills, "Viscosity of Electrolytes and Related Properties," Int. Encyclopedia of Phys. and Chem., Pergamon Press, New York (1965), p. 30.

[11] R. H. Stokes and R. Mills, Ioc. cit., p. 40.

solution is v' at the concentration C; then:

$$v = (1 - x)v_0 + xv' \tag{5}$$

where $v_0(\fallingdotseq 1/\rho_0)$ is the partial specific volume of the solvent in a solution. From Eqs. 4 and 5,

$$\rho/\rho_0 = 1 + (M\cdot C\cdot 10^{-3})(v_0 - v') \tag{6}$$

The effective volume, V, of the ions in solution is equal to $M\cdot v'\cdot 10^{-3}$ l./mol.

Experimental

All of substances used here were of an analytical reagent grade. Glycine was purified by recrystallization from an ethanol-water solution, and potassium chloride and urea, by recrystallization from conductivity water, but lithium chloride was used without further purification. Solutions from 0.05 to 0.25 molality were prepared. The systems of aqueous solutions were as follows:

System 1. Strong electrolytes: KCl and LiCl.

System 2. Weak electrolytes: Glycine and Urea.

System 3. Mixed electrolytes:

KCl + Glycine, KCl + Urea,
LiCl + Glycine, LiCl + Urea,

The viscosities of the solutions were measured at 15, 25 and 35±0.05°C by an Ostwald viscometer with a flow time of about 260 sec. for water at 25°C. The reproducibility of the flow times was within ±0.2 sec. Two viscometers were always used for a given system, and each measurement was repeated six to ten times and then the average was taken to get the desired result. By the measurement of the viscosity of water, dioxane and benzene, the correction term for kinetic energy was found to be so small that it was ignored. The relative viscosity was calculated by the usual formula:

$$\eta/\eta_0 = \frac{t(\text{flow time of solns.})\rho(\text{density of solns.})}{t_0(\text{flow time of water})\rho_0(\text{density of water})} \tag{7}$$

The densities of the solutions were measured by an Ostwald pycnometer of about 4 ml. The resistance of the solutions was measured with a universal bridge, Yokogawa BV-Z-13A. Three cells with platinized electrodes were used, their cell constants being 7.379, 1.445 and 0.8541, respectively; the electrodes were checked frequently with the 0.01 N or 0.1 N potassium chloride solutions. The data were reproducible within ±0.5%.

Results and Discussion

The relative and absolute viscosities of aqueous solutions of glycine and urea are given in Table I. Also, the relative viscosities of the mixed solutions are given in Figs. 1, 2 and 3.

Plotting $(\eta/\eta_0-1)/C^{1/2}$ versus $C^{1/2}$, the A coefficient is the ordinate intercept, while the B coefficient is given by the slope. The A and B coefficients thus obtained are summarized in Table II. Figures 1, 2 and 3 show that the relationship between the relative viscosities of the solution of mixed electrolytes and the concentration of the weak electrolytes is linear. The empirical formula of the relative viscosities (System 3) was obtained by the method of least squares; namely:

$$\eta = \eta' + \eta_0\beta C \tag{8}$$

TABLE I. RELATIVE AND ABSOLUTE VISCOSITIES OF AQUEOUS SOLUTIONS OF GLYCINE AND UREA AT 15, 25 AND 35°C

Glycine (m)	15°C		25°C		35°C	
	η/η_0	η (poise)	η/η_0	η (poise)	η/η_0	η (poise)
0	1.000	0.01144*	1.000	0.008949*	1.000	0.007208*
0.050	1.007	0.01152	1.007	0.009012	1.007	0.007258
0.100	1.013	0.01159	1.013	0.009065	1.014	0.007309
0.175	1.023	0.01171	1.024	0.009164	1.025	0.007388
0.250	1.034	0.01183	1.035	0.009262	1.036	0.007467
Urea (m)						
0.050	1.002	0.01147	1.002	0.008967	1.002	0.007222
0.100	1.004	0.01149	1.004	0.008985	1.004	0.007237
0.175	1.007	0.01152	1.007	0.009012	1.007	0.009012
0.250	1.009	0.01155	1.009	0.009030	1.010	0.00728

* Quoted from data of the International Critical Tables at each temp. (absolute viscosity of water)

TABLE II. COEFFICIENTS A AND B OF THE VISCOSITY EQ. 1

	15°C		25°C		35°C	
	A	B	A	B	A	B
LiCl	0.001	0.143	0.002	0.140	0.002	0.140
KCl	0.003	−0.037	0.003	−0.014	0.003	0.013
Glycine	0	0.136	0	0.140	0	0.143
Urea	0	0.037	0	0.037	0	0.040

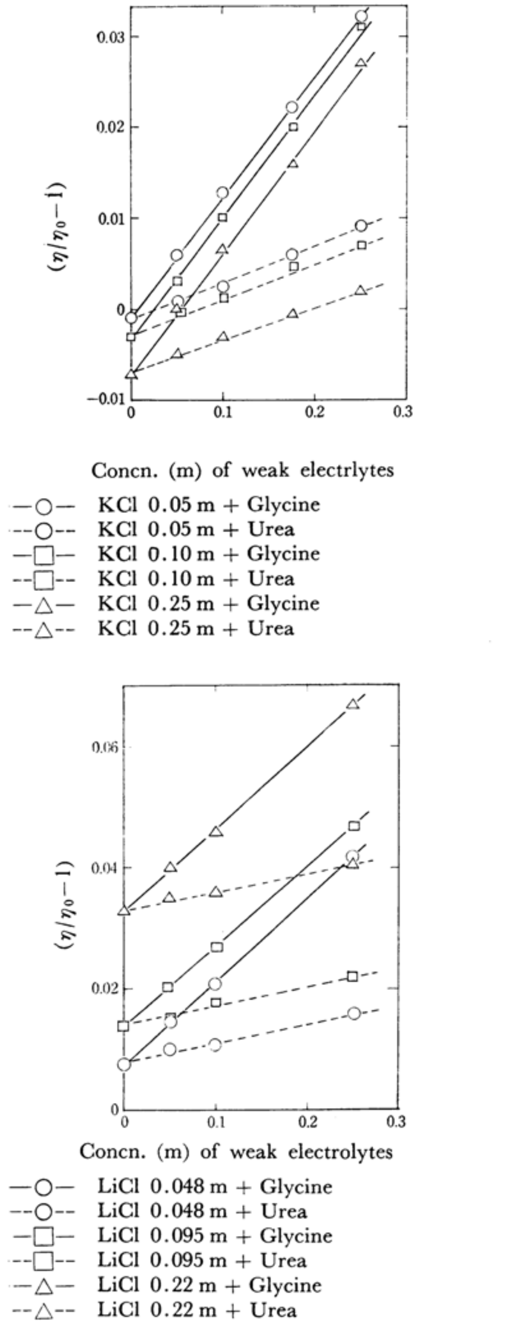


Fig. 1. Relative viscosities of mixed electrolyte solutions as a function of the concentration of added weak electrolyte, at 15°C.

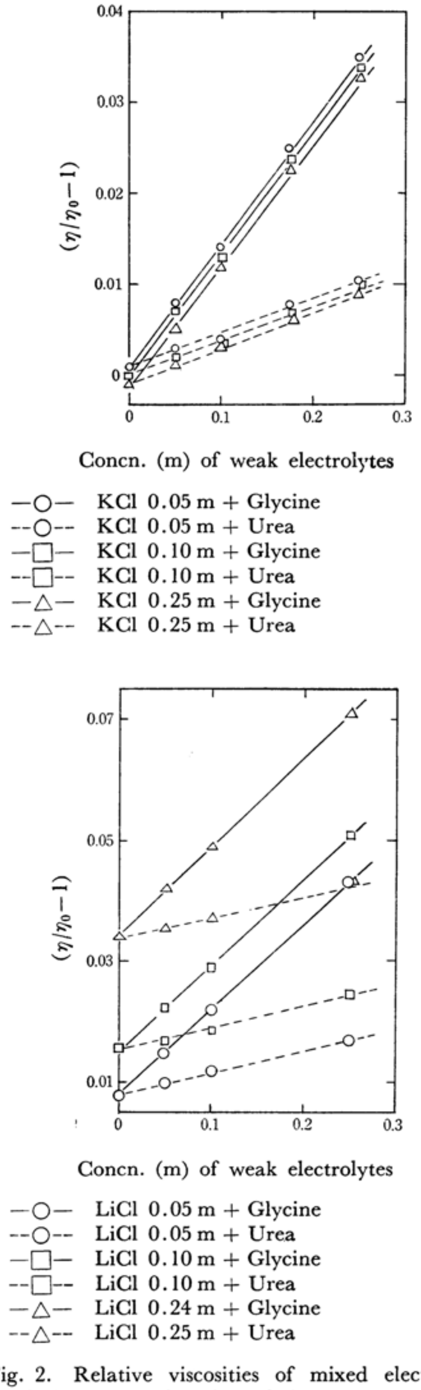


Fig. 2. Relative viscosities of mixed electrolyte solutions as a function of the concentration of added weak electrolyte, at 25°C.

where η' is the viscosity of the strong electrolyte at a given concentration, β is a constant characteristic of the weak electrolyte, and C is the molal concentration of the weak electrolyte. From the fact that the values of β thus found are nearly constant for a given weak electrolyte, as is shown in Figs. 1, and 2 and 3, the viscosity of weak electrolytes when mixed with strong electrolytes seems not to be influenced by the strong ones.

The specific gravities and the partial specific volumes of an aqueous solution of the weak electrolytes are given in Table III. In Fig. 4, a plot

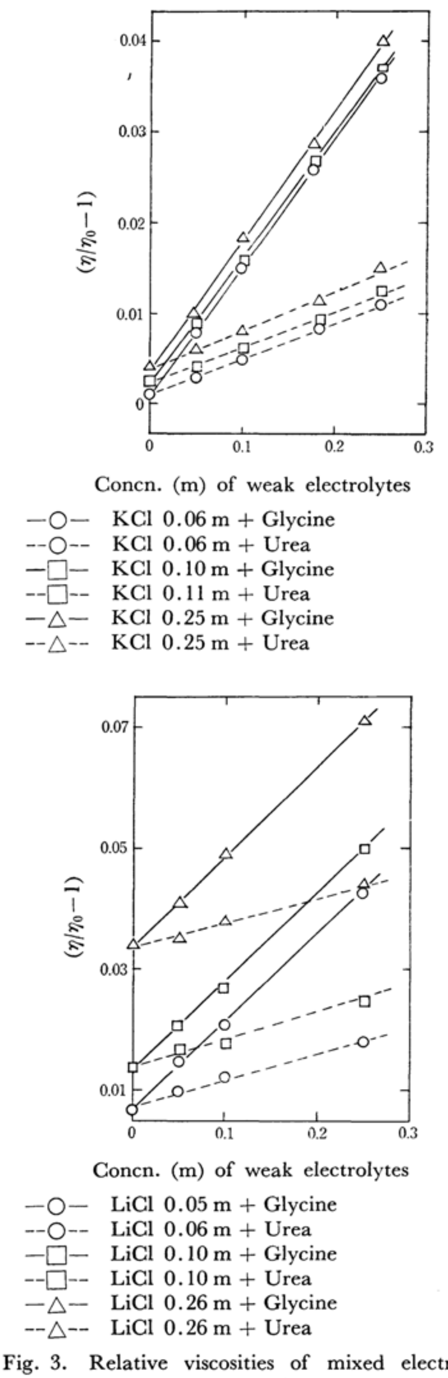
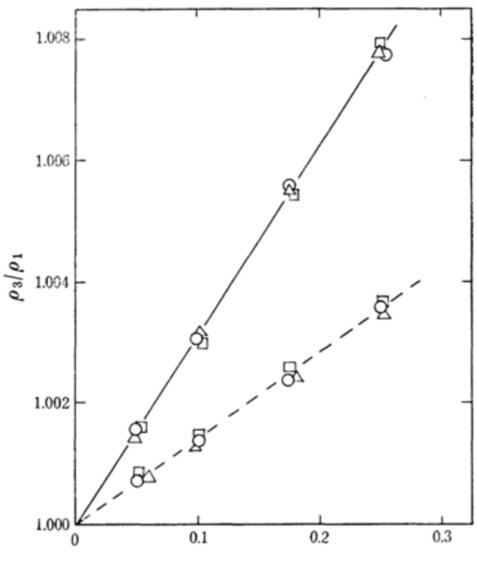


Fig. 3. Relative viscosities of mixed electrolyte solutions as a function of the concentration of added weak electrolyte, at 35°C.

of the ratio of the densities (ρ_3/ρ_1)* versus the concentration of the weak electrolyte gives a linear relation and is in accord with that of pure weak electrolyte solutions given in Table III. It is shown that the curves are independent of the temperature and species of the strong electrolyte used. From this fact, there seems to be little influence on the effective volume due to the electrostatic interaction between the ions and solutes of weak electrolytes, even though the solute is glycine, which has a comparatively large dipole moment,⁵⁾ in a polar solvent. Undoubtedly, the interaction between water molecules and all solutes in solution is more dominant than that between ions of the strong electrolyte and solutes of the weak one. It seems that the ions and the solutes in the mixed solution retain much the state of hydration they have in pure water, at least at the concentration considered.

The partial specific volumes of the electrolyte in solution are calculated from Eq. 5. The effective volumes(V) of ions in those solutions were estimated from the partial specific volume and are given in the third column of Table IV; other electrolytes quoted from the literature are given in the same column.

Let us assume that, for all the species thus obtained, the effective volume is a measure of the static volume occupied by the species in solution. Thus the B-values in the viscosity formula are considered to be the kinetic volumes of the solvated species in solution, and the values of the (B/V) ratio are considered to be closely related to the hydration. From Table IV it is apparent that the B/V values of alkaline halides, with the exception of lithium and sodium halides, are considerably different from



Concn. (mol./l.) of weak electrolyte (Glycine, Urea)

Fig. 4. Ratio of relative density as a function of the concentration of added weak electrolyte at 25°C.

(Coded as in Fig. 2. Full line: LiCl + Glycine
Broken line: LiCl + Urea

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* ρ_3 is the density of the mixed solution and ρ_1 is that of the strong electrolyte solution, the concentration of the strong electrolyte in both solutions being kept constant.

TABLE III. SPECIFIC GRAVITIES AND PARTIAL SPECIFIC VOLUMES OF AQUEOUS SOLUTIONS OF GLYCINE AND UREA AT 15, 25 AND 35°C

Glycine mol./l.	ρ/ρ_0	v'	Urea mol./l.	ρ/ρ_0	v'	Temp. °C
0.0498	1.0016	0.572	0.0498	1.0007	0.767	15
0.0995	1.0031	0.585	0.0995	1.0015	0.750	15
0.1735	1.0055	0.578	0.1735	1.0025	0.761	15
0.2471	1.0079	0.575	0.2469	1.0037	0.751	15
0.0497	1.0016	0.574	0.0497	1.0007	0.768	25
0.0993	1.0032	0.573	0.0992	1.0014	0.767	25
0.1731	1.0053	0.594	0.1731	1.0026	0.753	25
0.2466	1.0078	0.581	0.2465	1.0036	0.759	25
0.0496	1.0016	0.575	0.0496	1.0007	0.771	35
0.0990	1.0031	0.589	0.0990	1.0014	0.770	35
0.1726	1.0054	0.587	0.1726	1.0025	0.765	35
0.2459	1.0079	0.578	0.2457	1.0036	0.762	35

The values of ρ_0 were quoted from data of the International Critical Tables at each temperature.

TABLE IV. CONSTANTS OF DENSITY AND VISCOSTIY EQUATIONS AND HYDRATION NUMBER AT 25°C

Solute	V_c**	$V=Mv'10^{-3}$ l./mol.	B	B/V	Hydration number			
					(a)	(b)	(c)	(d)
LiCl	0.0206	0.0175	0.140	8.00	7.0	6	2.9—6.3	3.7—4.2
LiBr	0.0249	0.0249*	0.108[3]	4.34	7.6	5—6	2.9—5.6	—
LiI	0.0325	0.0363*	0.081[3]	2.23	2.0	—	—	—
NaCl	0.0268	0.0181*	0.079[3]	4.34	3.5	7	1.1—3.5	4.5—5.2
NaBr	0.0315	0.0245*	0.044[3]	1.80	4.2	6—7	1.2—2.8	—
NaI	0.0406	0.0358*	0.018[3]	0.50	5.5	—	2.2—3.0	—
KCl	0.0375	0.0278	−0.017	−0.61	1.9	7	0.6—0.8	3.6—4.3
KBr	0.0429	0.0349*	−0.048[3]	−1.38	2.1	6—7	0.3—1.2	—
KI	0.0528	0.0470*	−0.076[3]	−1.62	2.5	6—7	−0.3—1.5	—
RbCl	0.0438	0.0332*	−0.037[3]	−1.11	1.2	—	—	4.3—5.0
RbBr	0.0488	0.0402*	−0.072[3]	−1.79	0.9	—	—	—
RbI	0.0592	0.0516*	−0.099[3]	−1.92	0.6	—	—	—
CsCl	0.0424	0.0420*	−0.052[3]	−1.29	—	—	—	2.9—3.5
CsBr	0.0480	0.0472*	−0.087[3]	−1.84	—	—	—	—
CsI	0.0578	0.0580*	−0.113[3]	−1.93	—	—	—	—
$MgCl_2$	0.0410	0.0193*	0.371[3]	19.2	13.7	16—17	—	9.5—10.5
$CaCl_2$	0.0511	0.0218*	0.271[3]	12.4	12.0	10	—	9.2—10.3
$SrCl_2$	0.0519	0.0203*	0.251[3]	12.3	10.7	—	—	11.4—12.9
Glycine	0.0469	0.0435	0.140	3.22	—	—	—	2.7—3.4
Urea	0.0450	0.0457	0.036	0.79	—	—	—	—
Acetic acid	—	0.0514*	0.117[2]	2.28	—	—	—	—
Sucrose	—	0.2153*	0.879[1]	4.08	—	3.8	—	—

* The V-values were calculated by Eq. 6 from the data of densities in the International Critical Tables, their molal concentrations were from 0.05 to 0.25 m.

** The V_c values for inorganic salts were quoted from the International Critical Tables and the Kagaku Binran. For orgagnic compounds were quoted from the literature.[14]

(a) Ref. 1, (b) Ref. 12, (c) Ref. 8, (d) Ref. 13

those of alkaline earth metal chlorides, glycine and urea. Potassium, rubidium and cesium halides have negative B/V values. This will be discussed below. It is generally believed that the degree of hydration in aqueous electrolyte solutions decreases with an increase in the radius of the univalent cation.[2] Moreover, anions have the effect of breaking the structure of water.[3,4] As has been described previously, the ions with large crystal radii, such as Cs^+ or I^-, have a weak orienting effect in the first layer because of their small surface charge densities. Thus η^A would be small. However,

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[12] H. Shiio, *J. Am. Chem. Soc.*, **80**, 70 (1958).

[13] S. Goto and T. Isemura, This Bulletin, **37**, 1693 (1964).

[14] A. N. Winchell, "The Optical Properties of Organic Compounds," Academic Press Inc., Publishers, New York, N. Y. (1954).

a considerable distortion of the solvent structure may occur in the vicinity of the ion, and accordingly, η^D will become predominant. In this class of ions $\eta^A < \eta^D$ and the B/V value is negative. According to Samoilov,(15) the negative hydration was taken for the above case, and the molecules of water near the ion become more mobile than in pure water. On the other hand, as may be seen in Table IV, lithium chloride and alkaline earth metal chlorides produce a viscosity increment(16) greater than that corresponding to their effective volume in solution. The small size of cations with large surface charge densities, such as Li^+ and Mg^{2+}, cause a strong orientation of water molecules and they are believed to have a primary hydration. The η^E value will be large because of its primary sheath. The sum, $\eta^E + \eta^A$, will be larger than the decrement due to η^D. In this class, $\eta^A \gg \eta^D$ and the B/V value is fairly large and positive. Molecular ions such as glycine may be expected to have large η^E values because of their large size. As is shown in Table IV, the volume (V_c) of glycine in the crystal state is 0.0469 (l./mol.) and the effective volume (V) in solution is 0.0435 (l./mol.). This suggests that the behavior of glycine in hydration may resemble that of the strong electrolytes, such as lithium chloride, whose volume in a solution is apparently smaller than the volume in the crystal state due to the contraction of the solvent by electrostriction.(2) In addition, large η^A values may be expected from their large dipole moments, as has been pointed out already. However, the distortion effects would be the same as that of large ions mentioned above.

From the results obtained, it is evident that $\eta^A > \eta^D$ and that the B/V value for glycine is still positive. Isemura and Goto(17) have suggested, as a result of studies by the ultrasonic method, that glycine and strong electrolytes resemble each other in the mechanism of hydration; their suggestion is supported by the present results. The B/V values of urea is smaller than that of glycine, though the effective volume of urea, as may be seen in Table IV, is nearly equal to that of glycine. Again, we found that the V of urea in solution, as determined from the densities, is nearly equal to the volume(V_c) in the crystal state: V, 0.0457 (l./mol.); V_c, 0.0450 (l./mol.). It is well known that water molecules are attracted to the urea molecule, as urea has hydrophilic groups. From these findings, the hydration of urea can be interpreted as the result of competition between the breaking and the formation of the hydrogen bonding.

By means of measurements(13) of the NMR, the relative shifts of the proton resonances of aqueous solutions containing various electrolytes or organic compounds may be discussed with regard to their state of hydration. The results indicate that the degree of relative shifts of anions increase with an increase in the ionic radius. The differences in the B/V values in the lithium halides, therefore, seem to correspond with that of the relative shifts of anions, as they have a common cation in solution. Several methods,(8,12,13,16) from different standpoints and different assumptions, have been reported for determining the degree of hydration of electrolytes in an aqueous solution; these values are given in Table IV. The B/V values obtained may be compared with their hydration numbers, which are shown in the same table.

The relative conductivities of the mixed solutions are given in Figs. 5, 6 and 7. By plotting Λ/Λ_0 versus C, the γ coefficient is given by the slope. These figures show that the relative conductivities, Λ/Λ_0, are dependent on the concentration of the added weak electrolyte. Then, an empirical formula was obtained at each temperature, as follows:

$$\Lambda = \Lambda_0(1 - \gamma C) \tag{9}$$

TABLE V. γ-COEFFICIENT OF THE CONDUCTIVITY EQ. 9 AT EACH TEMPERATURE

	15°C	25°C	35°C
System 3.			
KCl + Glycine	0.127	0.130	0.128
LiCl + Glycine	0.120	0.129	0.130
KCl + Urea	0.068	0.075	0.076
LiCl + Urea	0.071	0.076	0.073

$\Lambda = \Lambda_0(1 - 0.127 \cdot C)$ for glycine,
$\Lambda = \Lambda_0(1 - 0.073 \cdot C)$ for urea.

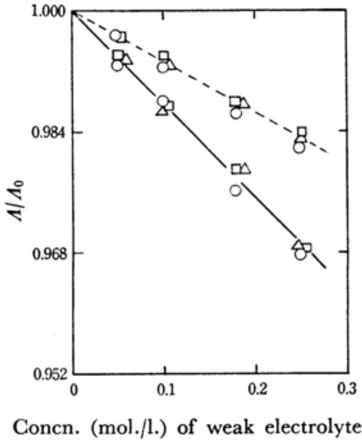

Fig. 5. Relative conductivities of mixed electrolyte solutions as a function of the concentration of added weak electrolyte, at 15°C.
Concn. of strong electrolyte:
○, 0.05 mol.; □, 0.10 mol.; △, 0.25 mol.

Full line: KCl + Glycine
Broken line: KCl + Urea
(Systems of lithium chloride are not given here, but their figures are nearly identical with the above systems.)

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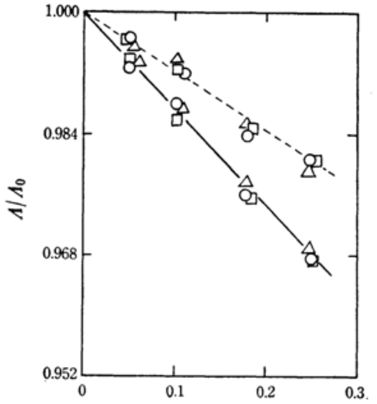
15) O. Ya. Samoilov, *Discussions Faraday Soc.*, **24**, 141 (1957).

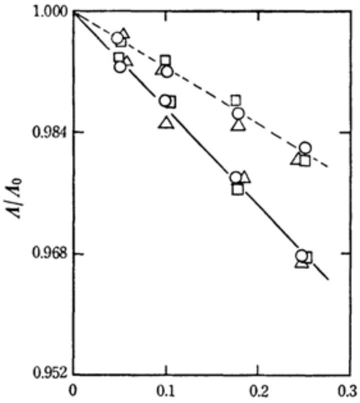
16) H. S. Frank and W. Y. Wen, ibid., **24**, 133 (1957).

17) T. Isemura and S. Goto, This Bulletin, **37**, 1697 (1964).



Concn. (mol./l.) of weak electrolytes

Fig. 6. Relative conductivities of mixed electrolyte solutions as a function of the concentration of added weak electrolyte, at 25°C. (Coded as in Fig. 5)



Concn. (mol./l.) of weak electrolytes

Fig. 7. Relative conductivities of mixed electrolyte solutions as a function of the concentration of added weak electrolyte, at 35°C. (Coded as in Fig. 5)

where Λ is the equivalent conductivity of the mixed solution; Λ_0 is that of a strong electrolyte in the pure solution, and γ is a constant characteristic of the added weak electrolyte. The γ coefficients thus obtained are summarized in Table V. From these results, it was found that the retarding effect of glycine on the ionic mobility of the strong electrolyte is greater than that of urea and that it is independent of the species of strong electrolyte used here. The ions of strong electrolytes, for example, are retarded to approximately the same extent when glycine is added to the solution at a given concentration. However, the viscosities of electrolytes are considerably different from each other. It seems that the retardation is independent of the frictional property of mixed solutions.