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Ultrasonic and Volumetric Investigation of Aqueous Solutions of Amides

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The ultrasonic velocity and density of aqueous solutions of *N*-methylformamide, *N,N*-dimethylformamide, and *N,N*-dimethylacetamide have been measured at 25 and 35 °C over the entire concentration range. The compressibility, excess compressibility, partial molar compressibility, partial molar volume, and pressure dependence of the partial molar volume have been calculated. The concentration dependences of the velocity and density are highly nonlinear, and the velocity maxima are observed in all the amide solutions at *ca.* 20 mol%. Minima in the partial molar volume exist in solutions of DMF and DMAA, but not in that of MFA. On taking account of the results for viscosity, the velocity maxima are ascribed to the complex formation, and the minima in the partial molar volume, to the competition between the volume increase due to the complex formation and the volume decrease due to the breaking-down of the water structure. The pressure dependence of the partial molar volume shows that amides and water have strong interactions, even in the low-mole-fraction regions for each component.

Numerous investigators have studied solute-solvent interaction in nonelectrolytic aqueous solutions from the point of view of their ultrasonic and volumetric behavior. In binary liquid mixtures, the nonlinear variation in the ultrasonic velocity with the concentration has been frequently observed, but the systems showing a velocity maximum are limited to aqueous solutions, except for the very rare case of the liquid paraffin–carbon tetrachloride system.

From among the many nonelectrolytes known to form aqueous solutions with a velocity maximum at a certain concentration, the present authors chose amides. The ultrasonic velocities and densities of aqueous solutions of *N*-methylformamide(MFA), *N,N*-dimethylformamide (DMF), and *N,N*-dimethylacetamide (DMAA) will be reported.

The aqueous solutions of amides have the following characteristic features concerning their ultrasonic and volumetric properties. First, the ultrasonic velocity and the density of pure amides have values similar to those of water. Secondly, in a solution of DMF, the maximum has been observed in the concentration dependence of the velocity as well as in that of the density. Nonelectrolytes showing a similar solution behavior include some kinds of amines (ethylenediamine and benzylamine[1]), acetic acid, dioxane,[2] and pyridine.[3]

The ultrasonic velocities in aqueous solutions of DMF[4] and DMAA[5] have been reported by Endo, and the densities of the aqueous solutions of DMF[6] and DMAA,[7] by Arakawa *et al.* and Assarsson and Eirich. We have undertaken the re-determination of the velocities and densities of these three aqueous solutions of amides in order to obtain consistent data. For instance, the density of DMAA given by Assarsson and Eirich[7] is 0.9350 g/ml at 25 °C. This value is not compatible with our result (0.9367_0 g/cm^3) nor with the value of 0.9366 g/cm^3 found in the literature.[8] The data by Assarsson and Eirich[7] are, as they themselves say, not accurate enough to establish whether or not a small minimum in the partial molar volume exists, as in alcohol–water systems, at a very low mole fraction of the amides.

Experimental

Materials. The MFA(guaranteed grade) and DMF (spectral grade), obtained respectively from the Tokyo Kasei Co., Ltd., and Nakarai Chemicals were used without further purification. The DMAA (guaranteed grade) was purified by distillation under reduced pressure.

Apparatus and Procedures. Measurements of the sound velocity were carried out at a fixed frequency of 4 MHz by means of an improved ultrasonic interferometer. This interferometer has the great advantage that a good parallelism between the reflector and the quartz surface can be attained by the aid of the screws and the springs, while in the interferometer used hitherto in our laboratory, the parallelism was mechanically determined. The parallelism is established by the application of the pulse-echo method. The measurement of the sound velocity was reproducible within 0.4 m/s. Further accuracy has been obtained by finely polishing the surface of the reflector. The density has been measured by using a 20-ml pycnometer. The density data are accurate to ±3 units in the fifth decimal place. Measurements were done at 25 and 35 °C.

Results and Discussion

Density and Velocity. The experimental results of the density and the ultrasonic velocity as a function of the composition are summarized in Tables 1—3. In all three aqueous solutions of amides studied in this work, the density as well as the ultrasonic velocity shows a high nonlinear dependence on the concentration. In the MFA system, the density maximum exists in the vicinity of 20 mol% of MFA. In the DMF and DMAA systems, sinuous but slight variations of the density have been observed in the low-concentration region of amide. After passing this region, the concentration dependence of the density is marked, but in a linear fashion. The aqueous solutions of alcohols, which exhibit a marked nonlinear dependence on the concentration in many physical properties, do not show such a clearly sinuous variation or a maximum point in relation to the concentration dependence of the density. All three amide systems show velocity maxima in the concentration range of 15—20 mol%, this range corresponds to the region where the decreases of density begin. The concentration dependence of the ultrasonic velocity in general, and also the position of the maximum, correspond well with the viscosity results of many kinds of aqueous solutions of amides.[7] Assarsson and Eirich, considering phase diagrams and heat of mixing in amide–water systems,[9] have related the observed maximum of viscosity to the formation of the complex. The veloc-

TABLE 1. DENSITY AND ULTRASONIC VELOCITY *vs.* COMPOSITION FOR THE *N*-METHYLFORMAMIDE (MFA)-WATER SYSTEM

	MFA (mol%)	Density (g/cm³)	Velocity (m/s)
At 25 °C	0.0	0.9970_4	$1496._3$
	2.265	1.000_0	$1527._5$
	5.958	1.004_7	$1563._2$
	12.12	1.010_7	$1595._4$
	19.57	1.014_3	$1606._7$
	24.02	1.015_7	$1602._7$
	35.19	1.015_7	$1577._7$
	48.38	1.012_7	$1536._3$
	66.97	1.007_0	$1487._7$
	79.79	1.003_4	$1460._9$
	100.00	0.9985_4	$1431._5$
At 35 °C	0.0	0.9940_3	$1519._5$
	6.258	1.000_6	$1570._6$
	11.90	1.004_9	$1590._5$
	17.36	1.007_5	$1594._2$
	24.42	1.009_1	$1586._0$
	35.10	1.008_4	$1556._2$
	50.66	1.004_4	$1507._9$
	67.64	0.9988_5	$1459._3$
	83.09	0.9943_6	$1431._0$
	100.00	0.9898_0	$1401._6$

TABLE 2. DENSITY AND ULTRASONIC VELOCITY *vs.* COMPOSITION FOR THE *N,N*-DIMETHYLFORMAMIDE (DMF)-WATER SYSTEM

	DMF (mol%)	Density (g/cm³)	Velocity (m/s)
At 25 °C	0.0	0.9970_4	$1496._3$
	1.724	0.9961_1	$1536._7$
	2.919	0.9960_4	$1560._6$
	7.072	0.9964_7	$1621._8$
	9.002	0.9965_8	$1642._5$
	14.51	0.9972_5	$1676._3$
	19.28	0.9964_0	$1688._3$
	24.01	0.9948_4	$1684._5$
	34.27	0.9876_3	$1661._3$
	49.77	0.9766_4	$1602._1$
	64.63	0.9651_3	$1548._8$
	79.21	0.9549_2	$1507._8$
	86.38	0.9506_5	$1487._5$
	100.00	0.9442_0	$1458._5$
At 35 °C	0.0	0.9940_3	$1519._5$
	1.724	0.9929_6	$1551._1$
	2.919	0.9923_2	$1569._7$
	6.179	0.9915_1	$1607._8$
	9.002	0.9910_2	$1631._3$
	15.82	0.9896_0	$1657._3$
	20.06	0.9881_6	$1659._9$
	23.98	0.9862_6	$1653._6$
	33.82	0.9797_5	$1626._3$
	49.13	0.9678_2	$1567._8$
	65.25	0.9552_3	$1509._9$
	80.01	0.9454_3	$1466._1$
	86.38	0.9414_2	$1448._5$
	100.00	0.9347_7	$1422._2$

TABLE 3. DENSITY AND ULTRASONIC VELOCITY *vs.* COMPOSITION FOR THE *N,N*-DIMETHYLACETAMIDE (DMAA)-WATER SYSTEM

	DMAA (mol%)	Density (g/cm³)	Velocity (m/s)
At 25 °C	0.0	0.9970_4	$1496._3$
	1.616	0.9956_4	$1546._3$
	3.060	0.9955_0	$1584._1$
	5.897	0.9965_7	$1641._8$
	8.229	0.9972_2	$1678._8$
	11.50	0.9985_1	$1711._3$
	18.14	0.9985_0	$1737._4$
	24.39	0.9959_2	$1730._9$
	36.81	0.9858_6	$1682._1$
	49.63	0.9739_1	$1626._1$
	66.25	0.9591_7	$1557._9$
	77.76	0.9502_6	$1517._7$
	85.58	0.9446_1	$1493._2$
	100.00	0.9367_0	$1462._6$
At 35 °C	0.0	0.9940_3	$1519._5$
	1.353	0.9926_0	$1554._1$
	2.541	0.9918_5	$1580._6$
	5.879	0.9914_0	$1636._8$
	7.762	0.9914_1	$1660._2$
	11.62	0.9915_6	$1690._6$
	16.76	0.9907_9	$1704._7$
	24.52	0.9869_1	$1693._6$
	35.69	0.9774_5	$1647._4$
	48.01	0.9657_6	$1591._4$
	68.38	0.9482_0	$1510._8$
	75.64	0.9426_9	$1485._7$
	89.92	0.9336_5	$1442._1$
	100.00	0.9274_3	$1418._9$

ity maximum has been reported in the aqueous solutions of tetrahydrofran, 1,4-dioxane, and *t*-butyl alcohol in the concentration range of 3—8 mol%.[10] These compounds form solid clathrates of 17 hydrates. In these cases, there is no doubt of the relationship between the occurrence of the velocity maximum and the formation of a "compound" (hydrate or other).

Generally speaking, the velocity maximum in solutions do not always necessiate the formation of a "compound." However, in the aqueous solutions of amides concerned in this work, the resemblance between the concentration dependence of the ultrasonic velocity and that of the viscosity indicates that the velocity maximum arises from the formation of the complex, therefore, the position of the velocity maximum indicate its composition. However, the structure of the complex formed in amide–water systems may not be similar to those in an ordinary clathrate like 17 hydrate or $8X\cdot 136H_2O$.

Compressibility. From the values of the velocity and density, the adiabatic comprssibility, κ_s has been calculated. The concentration dependence of κ_s is shown in Fig. 1. DMAA gives a similar dependence of the compressibility. Concerning Fig. 1 two facts should be mentioned: the appearance of the minimum and the temperature-independent point. The former

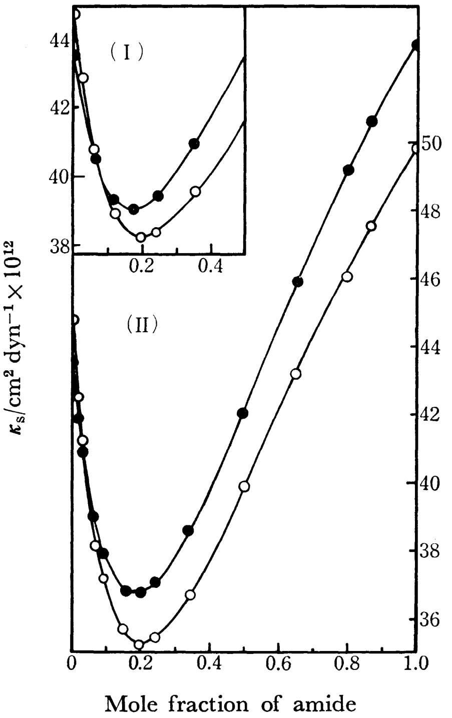

Fig. 1. Concentration dependence of adiabatic compressibility of the aqueous solutions of MFA (I) and DMF (II).
○: 25 °C, ●: 35 °C.

corresponds to the occurrence of the maximum in the velocity (and also in the density for the MFA system). The latter corresponds to the appearance of the common intersection in the relation of the temperature dependence of the velocity in solution. The phenomenon of the common intersection in the velocity has often been observed in many nonelectrolytic aqueous solutions.[4,5,11,12] Endo[4,5] has argued that this phenomenon is due to the clathrate formation and that the concentration of the common intersection should give the composition of the clathrate. The measurements of the ultrasonic velocity of Endo are quite extensive in terms of materials and the temperature range. However, his discussion of the common intersection has the crucial defect that comparisons with other properties which have intimate relations to the ultrasonic velocity, such as the density and the ultrasonic absorption coefficients, are disregarded. The relation between the common intersection and the partial molar volume will be discussed below.

The excess adiabatic compressibility, κ_s^E has been calculated from κ_s, and the molar volumes, V, of the mixtures and the pure components, A and B by means of this equation:

$$\kappa_s^E = \kappa_s - \frac{1}{V}(X_A V_A \kappa_{s,A} + X_B V_B \kappa_{s,B}).$$

The results are shown in the Fig. 2. κ_s^E's are always negative, and the values decrease as the $-CH_2-$ group increases. The temperature coefficients change their sign at a certain concentration in all systems.

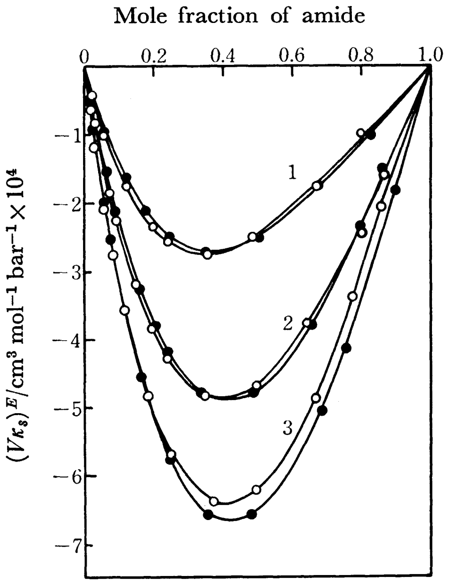

Fig. 2. Concentration dependence of excess compressibility of the amides solutions.
1: MFA–water system, 2: DMF–water system,
3: DMAA–water system.
○: 25 °C, ●: 35 °C.

Partial Molar Volume and Partial Molar Compressibility. From the density data given in Tables 1—3, the characteristic behavior of the partial molar volume of amides in solutions represented in Fig. 3 is obtained. The relation of the partial molar volume to the composition at 35 °C falls on the curves shown in Fig. 3. Similarly, as for κ_s^E, the curves become steeper as the number of the $-CH_2-$ group increases. The behavior of the aqueous solutions of amides shown in Fig. 3 closely resembles that of aqueous solutions of alcohols[13] and amines.[14] Sometimes the position of the minimum in the partial molar volume *vs.* composition relation roughly coincides with the common intersection of the ultrasonic velocity (therefore, the compressibility), for example, in aqueous solutions of tetramethylurea[11] and ethers.[12] The comparison of Fig. 1 with Fig. 3 shows that, for

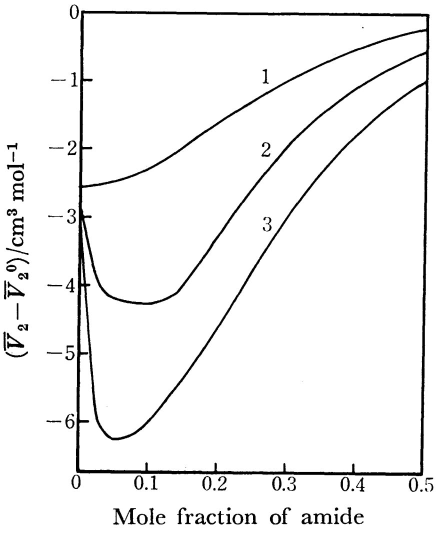

Fig. 3. Partial molar volume of amides in aqueous solution at 25 °C.
1: MFA, 2: DMF, 3: DMAA.

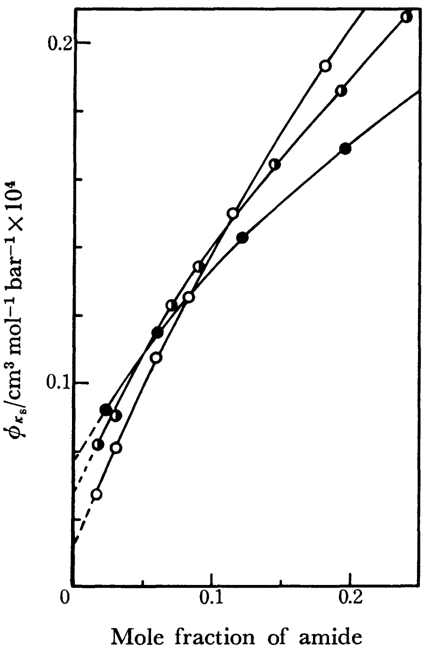

Fig. 4. Apparent molar compressibility of dilute aqueous solutions of amides at 25 °C.
●: MFA, ◐: DMF, ○: DMAA.

DMA and DMAA, this coincidence holds, but for MFA this is not the case.

Figure 4 shows the apparent molar compressibility, ϕ_{κ_s}, at 25 °C as calculated by means of this equation:

$$\phi_{\kappa_s} = \frac{1000(\kappa_s - \kappa_{s,1})}{c} + \kappa_{s,1}\phi_v,$$

where the subscript 1 refers to the solvent, c is the concentration in molarity, and ϕ_v is the apparent molar volume. According to Fig. 4, at an infinite dilution the ϕ_{κ_s} values are in this order: MFA, DMF, DMAA: that is to say, as a molecule has more $-CH_2-$ groups, the more rigid it becomes. The order of the rigidity, however, is inverted in the concentration range above *ca.* 10 mol%.

As an inversion of the order of the values of ϕ_{κ_s}, the common intersection in the ultrasonic velocity, and the minimum in the partial molar volume, occur in a similar region of the concentration, these phenomena may have some interrelations. However, any interpretations of these phenomena must be consistent with the appearances of the velocity maximum and the viscosity maximum observed in the concentration range beyond 20 mol%.

As has been mentioned above, the maximum in ultrasonic velocity has been ascribed to the complex formation. The following is a tentative interpretation of the partial molar volume as a function of the concentration. The complex formed by the hydrogen-bonding between amide and water has a rigid, but bulky structure. Therefore, the complex formation gives rise to an increase in the apparent volume of amide. The minimum in the partial molar volume may, then, be attributed to the competition between the volume increase due to the complex formation and the volume decrease due to the breaking-down of the water structure.

The relationship of the common intersection in the ultrasonic velocity with the other phenomena is not clear at present. The coincidence of the minimum position in the partial molar volume with the common intersection in the ultrasonic velocity is part of the complicated nature of the aqueous solutions. However, with regard to the aqueous solutions of amides studied in this work, the composition of the common intersection of the ultrasonic velocity can not be considered to indicate that of the "compound" formed in solution.

Pressure Dependence of the Partial Molar Volume.

For the partial molar volume of a solute, its pressure dependence can be calculated from the following equation:[16)]

$$\frac{\partial \bar{V}_2}{\partial p} = -\kappa \bar{V}_2 - (1-X)V\frac{\partial \kappa}{\partial X}.$$

The results of calculation are given in Fig. 5. In a dilute solution of amides, the three curves in Fig. 5 intersect with one another, and this intersection corresponds to the inversion of the order of ϕ_{κ_s} in Fig. 4. In a dilute region, $\partial \bar{V}_2/\partial p$ is very large. As the concentration of a solute increases, the variation in $\partial \bar{V}_2/\partial p$ gradually decreases. For small molecules, the variation in $\partial \bar{V}_2/\partial p$ with the concentration ceases in more dilute solutions than in case of large molecules, and in the pure state of amide, the order of $\partial \bar{V}_2/\partial p$ for the three systems is, as it should be, MFA, DMF, DMAA. The strong dependence of $\partial \bar{V}_2/\partial p$ on the concentration in a dilute aqueous solution of amides indicates the strong solute-solvent interaction in solution. Calculations using the data at 35 °C have given, for all three systems, more negative values than those shown in Fig. 5. The negative values of $\partial \bar{V}_2/\partial p$ are equivalent to the negative values of K_x, where K_x is the relative partial specific compression of the solute,[15)] and where the amide is taken as a solute. A negative K_x value signifies the non-existence of an incompressible region in the solution. However, this does not contradict with the complex formation between amides and water, because the hydrogen-bonding interactions are not so strong as to

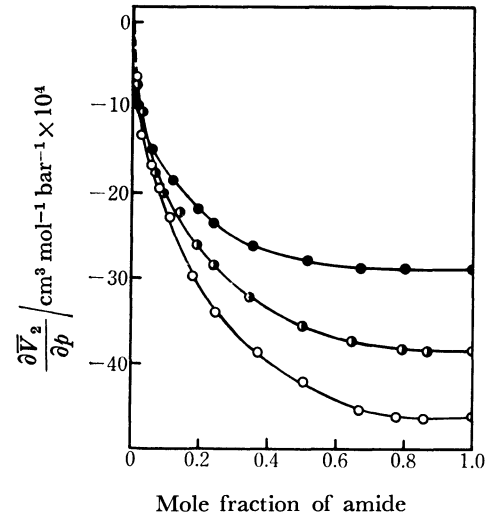

Fig. 5. Concentration dependence of $\partial \bar{V}_2/\partial p$ at 25 °C.
●: MFA–water system, ◐: DMF–water system,
○: DMAA–water system.

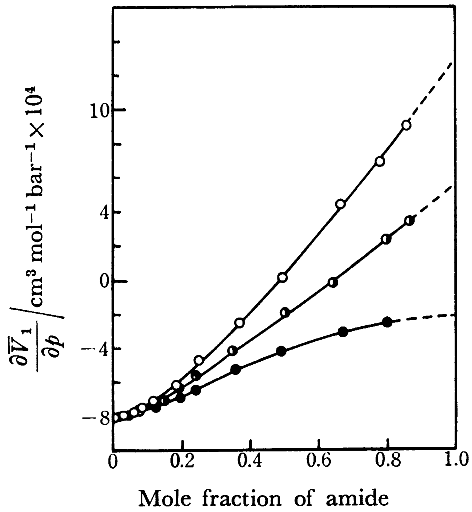

Fig. 6. Concentration dependence of $\partial\bar{V}_1/\partial p$ at 25 °C. ●: MFA–water system, ◐: DMF–water system, ○: DMAA–water system.

the coulombic ones typically observed in the form of ionic hydration.

The pressure dependence of the partial molar volume of the solvent can be obtained in a similar way; the results are shown in Fig. 6. The values of $\partial\bar{V}_1/\partial p$ and its concentration dependence are in the order of DMAA, DMF, and MFA. For solutions of DMAA and DMF, $\partial\bar{V}_1/\partial p$ are positive in the water-rich region. The marked dependence of $\partial\bar{V}_1/\partial p$ on the concentration in the water-rich region shows that, when a small amount of water is dissolved in amides, water molecules interact very strongly with amide molecules.

In summing up the results of Figs. 5 and 6, it is evident that strong interactions exist between water and amides, even in low-mole-fractions for each component.

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