

# Isentropic compressibilities of (amide + water) mixtures: A comparative study

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## Abstract

The density and ultrasonic velocity of aqueous solutions of formamide (FA), *N*-methylformamide (NMF), *N,N*-dimethylformamide (DMF), *N,N*-dimethylacetamide (DMA), pyrrolidin-2-one (PYR), *N*-methyl-2-pyrrolidinone (NMP), and their pure phases have been measured at 298.15 K and atmospheric pressure. Densities and ultrasonic velocities in pure amides have been also measured at the temperature range 288.15 K to 308.15 K for the computation of their thermal expansivities. Isentropic compressibility, intermolecular free length, relative association, apparent molar compressibility, as well as the excess quantities, ultrasonic velocity, isentropic compressibility, intermolecular free length, have been evaluated and fitted to the Redlich–Kister type equation. The deviation from ideal mixing law in ultrasonic velocity is positive while the deviations in isentropic compressibility and intermolecular free length are negative for all (amide + water) mixtures. This behavior reveals the nature and the magnitude of intermolecular interactions between the amide–water molecules. The sequence of superimposed curves of various ultrasonic parameters *vs.* the amide mole fraction is related to the strength of interactions between the unlike molecules and the role of  $-\text{CH}_3$  substitution in amides. The comparison of ultrasonic to volumetric properties reveals differences on the position of the extrema and their relation with the degree of substitution while the interpretation of these differences is discussed. Two different approaches on the computation of excess functions, applied in this work, brought out a difference in the magnitude of deviations and a partial reversion to the sequence of amides curves suggesting a different estimation in terms of deviations from ideal mixing law and therefore of the relative molecular interactions.

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**Keywords:** Ultrasonic velocity; Isentropic compressibility; Apparent molar compressibility; Formamide/water; *N*-Methylformamide/water; *N,N*-Dimethylformamide/water; *N,N*-Dimethylacetamide/water; *N*-Methyl-2-pyrrolidinone/water; (Pyrrolidin-2-one + water) mixtures; Excess quantities

## 1. Introduction

Among the different solvents, amides have a particular position in detecting the effect of solvents in the solutions of different substances. The interest in these solvents arises from a theoretical view as well as from the biological, pharmaceutical and other applications of pure solvents and their aqueous solutions. The volumetric properties of amide aqueous solutions have been extensively studied: formamide [1–5], *N*-methylformamide [5–7], *N,N*-dimethylformamide [3–5,7–10], *N,N*-dimethylacetamide [1–4,11–14],

pyrrolidin-2-one [5,7,15,16], *N*-methyl-2-pyrrolidinone [5,7,16–18]. The ultrasonic behavior of amides in water [4,9,16,19,20] or other solvent mixtures [21–25] has been also reported as well as their dielectric constants [15,26] and viscosity behavior [4,5,13,14,16–18,23,25]. Some of these amides have been involved in our studies [27] and invoked our interest to the detailed evaluation of their ultrasonic properties (ultrasonic velocity, isentropic compressibility, intermolecular free length, apparent molar compressibility) across the entire range of mole fractions. As far as we know, a systematic study of ultrasonic properties in (amide + water) mixtures is not available. The present work aims to provide a comparative study of the ultrasonic properties in aqueous solutions of the most used

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amides at ambient temperature which besides the well-studied volumetric properties would be a useful tool in elucidating the intermolecular and structural interactions among the water and amides molecules. Moreover, their knowledge would be useful in elucidating the ultrasonic behavior in various substances in the aqueous mixtures of these solvents and the role of interactions between solute–solvent molecules in these solutions.

Evidence for the interpretation of the experimental ultrasonic properties in the liquids mixtures provides the deviation from their ideal values. Various approaches [28–33] have been used for the calculation of ideal ultrasonic velocity or ideal isentropic compressibility and other thermodynamics properties. Therefore, the evaluation of their excess values and the investigation in the light of new approaches [28,29], based on a detailed thermodynamical formulation, are very significant for the interpretation of molecular interactions and critical for the comparison of the behavior of various solvents.

## 2. Experimental

The solvents were supplied: formamide (stated purity >99%-microselect for molecular biology), *N*-methylformamide (stated purity >99%), *N,N*-dimethylformamide (stated purity >99.8%), *N,N*-dimethylacetamide (stated purity >99.5%), *N*-methyl-2-pyrrolidinone (stated purity >99%) by Fluca, pyrrolidin-2-one (stated purity >99%) by Acros, and were used without other purification. The solvents were kept over molecular sieves. The water was deionized and distilled prior to be used for making up solutions or calibrations. Its conductivity at 298.15 K was  $0.7 \cdot 10^{-6} \Omega^{-1} \text{cm}^{-1}$ . Densities were measured at 298.15 K with a vibrating tube digital densimeter (Anton Paar-DMA 58). The precision of density reading was within  $\pm 0.5 \cdot 10^{-5} \text{g cm}^{-3}$ , the accuracy  $\pm 1 \cdot 10^{-5} \text{g cm}^{-3}$  and the temperature was kept constant within 0.01 K by an internal Peltier element of the apparatus. Ultrasonic velocities were measured at 298.15 K with a digital sound analyzer (Anton Paar-DSA 48). The precision of readings was  $\pm 0.1 \text{ms}^{-1}$ , the accuracy  $\pm 1 \text{ms}^{-1}$  and the temperature was kept constant within 0.01 K. Both apparatus cells were calibrated with dry air and distilled water at the beginning of every set of experiments. Densities and ultrasonic velocities in pure water and solvents were compared with the literature values to confirm their purity and temperature constancy, tables 1 and 2, respectively.

All binary aqueous mixtures (amide/W) were prepared by mass covering the whole region from 0% to 100% in solvent.

## 3. Results and discussion

Densities  $\rho$  and ultrasonic velocity  $u$  have been measured for all pure amides and their binary aqueous mixtures at 298.15 K across the entire range of mole fractions. From these data isentropic compressibility  $\kappa_s$ ,

of pure amides and (amide + water) mixtures were calculated [28,40] from the Newton–Laplace equation:

$$\kappa_s = \frac{1}{u^2 \rho} \quad (1)$$

In addition various thermodynamics parameters as apparent molar compressibility  $\kappa_\phi$  [41a,42], intermolecular free length  $L_f$  [24,25,46], relative association  $R_A$  [43,45], were calculated. The following relations have been used

$$L_f = K(\kappa_s)^{1/2} \quad (2)$$

$$R_A = \frac{\rho}{\rho_1^*} \left( \frac{u_1^*}{u} \right)^{1/3} \quad (3)$$

$$\kappa_{\phi,2} = \frac{\kappa_s M_2}{\rho} + \frac{(\kappa_s \rho_1^* - \kappa_{s,1}^*)}{m_2 \rho \rho_1^*} \quad (4)$$

where  $\rho_1^*$ ,  $\rho_2^*$ ,  $\rho$ , and  $u_1^*$ ,  $u_2^*$ ,  $u$  are the densities and the ultrasonic velocities in water, amide, and solution, respectively,  $M_2$  is the molar mass of the amide,  $m_2$  the molality of amide,  $\kappa_{s,1}^*$ ,  $\kappa_{s,2}^*$ ,  $\kappa_s$  are the isentropic compressibility of water, amide, and solution, respectively, and  $K$  is the Jacobson's temperature dependent-constant. The value of  $K$  is computed from the  $K = (76.551 + 0.4039T) \cdot 10^{-8}$  obtained by linear fitting of data of reference [46]. The reported data of  $K$  have been corrected by a coefficient arising from the calculated values of  $L_f$  of various liquids reported in this reference. At  $T = 298.15 \text{K}$ , the constant  $K$  has the value  $196.97 \cdot 10^{-8} \text{N}^{1/2}$  which is comparable with values used in the literature [24,25,44,46].

The values of  $\rho$ ,  $u$ ,  $\kappa_s$ ,  $L_f$ , are listed in table 3.

In the attempt to get insight in the intermolecular interactions that are present in these mixtures, various excess functions were calculated. The excess thermodynamic quantities  $Y^E$  represent the deviation of experimental values from those of an ideal mixture  $Y^{\text{id}}$  of the same solvents and were calculated from the relation:

$$Y^E = Y - Y^{\text{id}} \quad (5)$$

where  $Y^E$  denotes the excess thermodynamic quantity as excess molar volume  $V^E$ , excess ultrasonic velocity  $u^E$ , excess isentropic compressibility  $\kappa_s^E$ , excess intermolecular free length  $L_f^E$  and  $Y^{\text{id}}$  is their respective ideal quantity defined by the ideal mixing law.

The ideal isentropic compressibility  $\kappa_s^{\text{id}}$ , evaluated from ideal mixing rule for constant pressure and temperature [25,26], is given by the equation:

$$\kappa_s^{\text{id}} = \phi_1 \kappa_{s,1}^* + \phi_2 \kappa_{s,2}^* + \left[ \frac{\phi_1 V_1^* (a_{P,1}^*)^2}{C_{P,1}^*} + \frac{\phi_2 V_2^* (a_{P,2}^*)^2}{C_{P,2}^*} - \frac{V_m^{\text{id}} (a_P^{\text{id}})^2}{C_{P,m}^{\text{id}}} \right] \quad (6)$$

where  $\phi_i$  the ideal volume fraction ( $=x_i V_i^*/V_m^{\text{id}}$ ) of the components,  $V_i^*$ ,  $\alpha_{P,i}^*$ ,  $C_{P,i}^*$  are the molar volume, the thermal expansibility and the molar heat capacity at constant pressure of pure components, respectively and  $V_m^{\text{id}}$ ,  $\alpha_P^{\text{id}}$ ,  $C_{P,m}^{\text{id}}$  are the respective ideal mixing quantities. The subscripts 1 and 2 are referred to water and amide, respectively.

TABLE 1  
Densities  $\rho/(\text{g} \cdot \text{cm}^{-3})$  of water and pure amides at 298.15 K

W	FA	NMF	DMF	DMA	PYR	NMP
0.99704 <sup>a</sup>	1.12901 <sup>a</sup> [27]	0.99906 <sup>a</sup>	0.94394 <sup>a</sup>	0.93634 <sup>a</sup>	1.10697 <sup>a</sup>	1.02823 <sup>a</sup>
0.997047 [34]	1.129797 [1]	0.99929 [5]	0.94406 [5]	0.936076 [1]	1.10747 [5]	1.02832 [5]
	1.129155 [2]	0.998244 [6],[20]	0.94383 [7]	0.936337 [2]	1.10643 [7]	1.02759 [7]
	1.12975 [5]	0.99889 [7]	0.943761 [8]	0.93615 [12]	1.10701 [15]	1.0286 [13]
	1.12919 [19]	0.99876 [27]	0.942915 [10]	0.9350 [13]	1.107019 [16]	1.028311 [16]
	1.12915 [35]	0.998319 [36]	0.94420 [20]	0.9365 [25]		1.0283 [17]
			0.9446 [24]	0.935287 [11]		1.02872 [18]
			0.99404 [27]			
			0.943320 [36]			
			0.943915 [37]			

<sup>a</sup> Used in this work.

TABLE 2  
Ultrasonic velocities  $u/(\text{m} \cdot \text{s}^{-1})$  in water and pure amides at 298.15 K

W	FA	NMF	DMF	DMA	PYR	NMP
1496.98 <sup>a</sup>	1597.79 <sup>a</sup>	1431.21 <sup>a</sup>	1457.49 <sup>a</sup>	1455.91 <sup>a</sup>	1633.95 <sup>a</sup>	1546.06 <sup>a</sup>
1498.0 [16]	1599.05 [19]	1431.5 [20]	1458.5 [20]	1462.0 [25]	1633.2 [16]	1545.1 [16]
1496.68 [39]			1468.0 [24]			
			1457.30 [37]			

<sup>a</sup> Used in this work.

The thermodynamic ideal mixing rules for the ideal mixing quantities  $V_m^{\text{id}}$ ,  $\alpha_p^{\text{id}}$ ,  $C_{p,m}^{\text{id}}$  of the mixture are defined [28] by the equations:

$$V_m^{\text{id}} = \sum_i x_i V_i^*, \quad \alpha_p^{\text{id}} = \sum_i \phi_i \alpha_{p,i}^*,$$

$$C_{p,m}^{\text{id}} = \sum_i x_i C_{p,i}^*, \quad \rho^{\text{id}} = \sum_i \phi_i \rho_i^* \quad (7)$$

where  $x_i$  the mole fraction ( $=n_i/\sum n_i$ ) of components.

The ultrasonic velocity  $u^{\text{id}}$  and intermolecular free length  $L_f^{\text{id}}$  in an ideal liquid mixture are calculated, respectively, by the equation:

$$u^{\text{id}} = \frac{1}{(\rho^{\text{id}} \kappa_s^{\text{id}})^{1/2}} = \left[ \frac{V_m^{\text{id}}}{M_m \kappa_s^{\text{id}}} \right]^{1/2} \quad (8)$$

$$L_f^{\text{id}} = K(\kappa_s^{\text{id}})^{1/2} \quad (9)$$

where  $M_m = x_1 M_1^* + x_2 M_2^*$  ( $M_1^*$ ,  $M_2^*$  the molar masses of pure components).

The change of a thermodynamic quantity  $\Delta Y$  due to mixing of pure components is expressed by the equation:

$$\Delta Y = Y - \sum_i x_i Y_i^* \quad (10)$$

and it is frequently used to approximate deviations from ideality.  $\Delta u$  and  $\Delta L_f$  are calculated from equation (10) and compared with their respective excess properties  $u^E$ ,  $\kappa_s^E$  which properly express the molecular interactions. A similar equation to (10) is used for the calculation of  $\Delta \kappa_s$  where the mole fraction  $x_i$  is substituted by the volume fraction  $\phi_i$ .

The evaluation of excess quantities require the knowledge of molar heat capacities at constant pressure  $C_p$  (table 4) and thermal expansibilities  $\alpha_p$  at constant pressure

(atmospheric) of pure amides at 298.15 K (table 5). Molar heat capacities were obtained from the literature while thermal expansibilities were computed [34,38,41b] from density measurements at various temperatures in the range (288.15 to 308.15) K (table 6) by the equation:

$$\alpha_p = - \left( \frac{\partial \ln \rho}{\partial T} \right)_p \quad (11)$$

The values of the excess functions  $V^E$ ,  $u^E$ ,  $\kappa_s^E$ ,  $L_f^E$  are listed in table 7.

The excess functions  $Y^E$  ( $V^E$ ,  $u^E$ ,  $\kappa_s^E$ ) were fitted to the Redlich–Kister type equation, and are listed in table 8, along with the standard deviation  $\sigma_Y$ :

$$Y^E = x_2(1-x_2) \sum_{i=1}^5 A_i(1-2x_2)^{i-1} \quad (12)$$

$$\sigma_Y = \left[ \frac{\sum (Y_{\text{exp}}^E - Y_{\text{cal}}^E)^2}{n_{\text{exp}} - n} \right]^{1/2} \quad (13)$$

where  $x_2$  the amide mole fraction,  $Y_{\text{exp}}^E$ , the values of the excess quantities derived from experimental values using the equation (6) and  $Y_{\text{cal}}^E$  the values calculated from the Redlich–Kister equation with the use of coefficients  $A_i$ ,  $n_{\text{exp}}$  the number of measurements and  $n$  the number of coefficients  $A_i$  in equation (12). A similar equation to (12) is used for the calculation of  $\kappa_s^E$  where the mole fraction  $x_i$  is substituted by the volume fraction  $\phi_i$ .

The ultrasonic properties in (amide + water) mixtures exhibit a maximum in ultrasonic velocity (table 3) and a minimum in isentropic compressibility (figure 1) and intermolecular free length (table 3) except in the case of FA/W where these properties monotonically change. This behavior indicates significant interactions between amide and

TABLE 3

Densities  $\rho$ , ultrasound velocities  $u$ , isentropic compressibilities  $\kappa_s$  and intermolecular free lengths  $L_f$ , of binary mixtures of FA, NMF, DMF, DMA, PYR, NMP with water versus amide mole fraction  $x_2$  at 298.15 K

$x_2$	$\rho/(\text{g} \cdot \text{cm}^{-3})$	$u/(\text{m} \cdot \text{s}^{-1})$	$\kappa_s/(\text{TPa}^{-1})$	$L_f/(\text{\AA})$
<i>Formamide</i>				
0.00000	0.99702	1497.03	447.54	0.4351
0.01258	1.00158	1506.97	439.65	0.4313
0.01991	1.00413	1512.23	435.49	0.4292
0.03610	1.00948	1522.77	427.20	0.4251
0.05028	1.01393	1530.90	420.82	0.4219
0.06473	1.01825	1538.28	415.03	0.4190
0.07977	1.02253	1545.12	409.64	0.4163
0.09437	1.02649	1551.04	404.95	0.4139
0.11246	1.03116	1557.54	399.76	0.4112
0.13468	1.03654	1564.45	394.18	0.4084
0.15959	1.04219	1570.97	388.79	0.4056
0.19461	1.04941	1578.29	382.54	0.4023
0.22952	1.05608	1584.06	377.36	0.3996
0.25478	1.06055	1587.46	374.17	0.3979
0.27310	1.06360	1589.49	372.14	0.3968
0.29195	1.06661	1591.37	370.21	0.3958
0.33428	1.07290	1594.66	366.53	0.3938
0.37110	1.07791	1596.71	363.89	0.3924
0.40457	1.08213	1598.07	361.85	0.3913
0.45522	1.08806	1599.44	359.26	0.3899
0.48842	1.09160	1600.00	357.85	0.3891
0.50252	1.09305	1600.15	357.30	0.3888
0.52247	1.09497	1600.34	356.59	0.3884
0.55641	1.09827	1600.50	355.45	0.3878
0.59496	1.10168	1600.54	354.33	0.3872
0.62975	1.10465	1600.45	353.42	0.3867
0.67139	1.10795	1600.24	352.46	0.3861
0.70199	1.11028	1600.03	351.81	0.3858
0.72296	1.11182	1599.82	351.42	0.3856
0.75440	1.11399	1599.64	350.81	0.3852
0.77998	1.11576	1599.41	350.36	0.3850
0.80943	1.11767	1599.14	349.88	0.3847
0.83576	1.11942	1598.85	349.46	0.3845
0.87518	1.12179	1598.58	348.83	0.3842
0.91702	1.12423	1598.23	348.23	0.3838
0.94653	1.12598	1598.01	347.78	0.3836
0.97025	1.12729	1597.88	347.44	0.3834
1.00000	1.12878	1597.28	347.24	0.3833
<i>N-Methylformamide</i>				
0.00000	0.99702	1497.03	447.54	0.4351
0.01572	0.99910	1518.74	433.93	0.4285
0.03276	1.00138	1538.85	421.70	0.4224
0.05095	1.00360	1557.22	410.90	0.4169
0.07104	1.00591	1574.12	401.20	0.4120
0.09226	1.00787	1582.73	396.08	0.4093
0.11557	1.01010	1591.27	390.97	0.4067
0.14098	1.01191	1601.56	385.28	0.4037
0.17144	1.01358	1606.06	382.49	0.4023
0.20054	1.01489	1606.15	381.95	0.4020
0.23391	1.01573	1603.41	382.94	0.4025
0.27138	1.01631	1598.79	384.94	0.4035
0.30468	1.01634	1594.03	387.23	0.4047
0.31855	1.01628	1589.32	389.55	0.4060
0.33674	1.01630	1583.72	392.30	0.4074
0.36149	1.01586	1572.98	397.85	0.4103
0.38530	1.01545	1560.74	404.28	0.4136
0.41658	1.01447	1551.93	409.28	0.4161
0.44559	1.01364	1542.90	414.42	0.4187
0.47853	1.01283	1534.22	419.46	0.4213
0.51092	1.01192	1526.39	424.15	0.4236

TABLE 3 (continued)

$x_2$	$\rho/(\text{g} \cdot \text{cm}^{-3})$	$u/(\text{m} \cdot \text{s}^{-1})$	$\kappa_s/(\text{TPa}^{-1})$	$L_f/(\text{\AA})$
0.54968	1.01088	1514.67	431.19	0.4271
0.58048	1.01004	1507.48	435.67	0.4293
0.59133	1.00949	1502.62	438.73	0.4308
0.61641	1.00890	1497.20	442.17	0.4325
0.63352	1.00822	1493.09	444.91	0.4338
0.68098	1.00672	1480.58	453.13	0.4378
0.73228	1.00535	1469.02	460.92	0.4416
0.77901	1.00451	1462.89	465.18	0.4436
0.82792	1.00334	1454.50	471.11	0.4464
0.85347	1.00254	1449.50	474.75	0.4482
0.87627	1.00172	1446.45	477.14	0.4493
0.91695	1.00103	1441.10	481.02	0.4511
0.92850	1.00072	1440.17	481.79	0.4515
1.00000	0.99906	1431.91	488.18	0.4545
<i>N,N-Dimethylformamide</i>				
0.00000	0.99702	1497.03	447.54	0.4351
0.01233	0.99644	1526.32	430.78	0.4269
0.02660	0.99621	1555.74	414.74	0.4189
0.02760	0.99623	1554.23	415.54	0.4193
0.04154	0.99618	1582.28	400.95	0.4119
0.05803	0.99638	1607.43	388.43	0.4054
0.07593	0.99662	1628.75	378.23	0.4000
0.09542	0.99684	1647.50	369.59	0.3954
0.11728	0.99702	1658.97	364.43	0.3927
0.14116	0.99693	1675.47	357.32	0.3888
0.16771	0.99602	1684.58	353.79	0.3869
0.19751	0.99510	1688.25	352.58	0.3862
0.23003	0.99387	1687.82	353.20	0.3866
0.28661	0.99018	1676.62	359.27	0.3899
0.31385	0.98917	1669.27	362.81	0.3918
0.37711	0.98428	1647.66	374.24	0.3979
0.42474	0.98119	1629.09	384.02	0.4031
0.44936	0.97947	1620.30	388.88	0.4056
0.47547	0.97779	1610.07	394.52	0.4085
0.49546	0.97640	1599.49	400.32	0.4115
0.52028	0.97498	1592.00	404.69	0.4138
0.53357	0.97417	1585.66	408.27	0.4156
0.55499	0.97269	1572.13	415.96	0.4195
0.58057	0.97092	1565.77	420.11	0.4216
0.61685	0.96890	1559.02	424.64	0.4238
0.63702	0.96732	1550.47	430.03	0.4265
0.65512	0.96583	1545.24	433.62	0.4283
0.69306	0.96335	1538.21	438.72	0.4308
0.71724	0.96178	1527.74	445.48	0.4341
0.73729	0.96060	1519.67	450.77	0.4367
0.75301	0.95956	1514.80	454.17	0.4383
0.76664	0.95873	1512.32	456.05	0.4392
0.80367	0.95619	1504.31	462.15	0.4422
0.81258	0.95554	1501.17	464.40	0.4432
0.84695	0.95357	1493.03	470.45	0.4461
0.86943	0.95212	1491.40	472.19	0.4470
0.89110	0.95068	1488.38	474.83	0.4482
0.92495	0.94801	1476.61	483.79	0.4524
0.96614	0.94628	1469.12	489.63	0.4551
1.00000	0.94394	1457.49	498.71	0.4593
<i>N,N-Dimethylacetamide</i>				
0.00000	0.99702	1497.03	447.54	0.4351
0.00083	0.99694	1499.79	445.93	0.4343
0.00163	0.99687	1502.39	444.42	0.4336
0.03959	0.99584	1616.25	384.41	0.4033
0.05500	0.99637	1645.53	370.65	0.3960
0.06456	0.99662	1663.23	362.72	0.3917
0.08126	0.99729	1678.58	355.87	0.3880

TABLE 3 (continued)

$x_2$	$\rho/(\text{g} \cdot \text{cm}^{-3})$	$u/(\text{m} \cdot \text{s}^{-1})$	$\kappa_s/(\text{TPa}^{-1})$	$L_f/(\text{\AA})$
0.10004	0.99794	1700.27	346.62	0.3829
0.12077	0.99850	1717.94	339.34	0.3789
0.14474	0.99868	1730.72	334.29	0.3761
0.17135	0.99855	1737.89	331.58	0.3745
0.20119	0.99761	1749.38	327.54	0.3723
0.23807	0.99572	1734.50	333.82	0.3758
0.27612	0.99203	1719.69	340.86	0.3797
0.32450	0.98832	1703.57	348.64	0.3841
0.37834	0.98512	1682.06	358.78	0.3896
0.41368	0.98241	1668.95	365.44	0.3932
0.45195	0.97926	1653.42	373.54	0.3975
0.48319	0.97557	1638.16	381.97	0.4020
0.53716	0.96973	1605.36	400.13	0.4114
0.58304	0.96529	1586.76	411.45	0.4172
0.64962	0.95934	1559.24	428.75	0.4259
0.70744	0.95342	1534.23	445.59	0.4342
0.76331	0.94972	1521.98	454.56	0.4385
0.83424	0.94612	1489.00	476.72	0.4491
0.90531	0.94096	1482.20	483.74	0.4524
1.00000	0.93634	1455.91	503.85	0.4617

*Pyrrolidin-2-one*

0.00000	0.99702	1497.03	447.54	0.4351
0.03793	1.01526	1577.37	395.87	0.4092
0.05001	1.02061	1597.62	383.88	0.4030
0.07966	1.03248	1632.11	363.60	0.3922
0.10930	1.04293	1670.03	343.79	0.3814
0.12204	1.04678	1684.53	336.66	0.3774
0.15820	1.05677	1708.04	324.36	0.3704
0.17894	1.06224	1716.48	319.52	0.3677
0.21554	1.07034	1726.63	313.39	0.3641
0.23523	1.07491	1732.07	310.10	0.3622
0.24730	1.07708	1735.25	308.34	0.3612
0.27938	1.08192	1737.27	306.25	0.3599
0.34972	1.08862	1735.45	305.00	0.3592
0.41989	1.09346	1727.83	306.33	0.3600
0.50134	1.09741	1715.75	309.54	0.3619
0.54904	1.09918	1708.84	311.55	0.3630
0.61328	1.10160	1698.72	314.58	0.3648
0.67049	1.10282	1683.44	319.96	0.3679
0.70374	1.10316	1678.52	321.74	0.3689
0.81170	1.10588	1658.04	328.93	0.3730
0.83527	1.10612	1654.56	330.24	0.3738
0.85927	1.10638	1651.32	331.46	0.3745
0.88132	1.10659	1647.92	332.77	0.3752
0.94127	1.10713	1640.70	335.54	0.3768
1.00000	1.10752	1633.68	338.31	0.3783

*N-Methyl-2-pyrrolidinone*

0.00000	0.99702	1497.03	447.54	0.4351
0.02533	1.00451	1573.56	402.05	0.4124
0.06006	1.01428	1646.77	363.56	0.3922
0.08026	1.02063	1684.39	345.34	0.3822
0.10081	1.02571	1724.66	327.77	0.3724
0.11909	1.03016	1731.16	323.91	0.3702
0.13994	1.03469	1745.21	317.32	0.3664
0.15956	1.03809	1747.65	315.40	0.3653
0.17789	1.04014	1749.21	314.21	0.3646
0.19637	1.04152	1751.66	312.92	0.3638
0.22033	1.04298	1750.72	312.82	0.3638
0.23986	1.04435	1750.14	312.61	0.3637
0.26016	1.04570	1745.27	313.96	0.3644
0.27803	1.04600	1741.84	315.10	0.3651
0.29867	1.04627	1735.38	317.37	0.3664
0.32961	1.04623	1725.58	321.00	0.3685

TABLE 3 (continued)

$x_2$	$\rho/(\text{g} \cdot \text{cm}^{-3})$	$u/(\text{m} \cdot \text{s}^{-1})$	$\kappa_s/(\text{TPa}^{-1})$	$L_f/(\text{\AA})$
0.37937	1.04576	1707.82	327.86	0.3724
0.44973	1.04433	1687.12	336.41	0.3773
0.49861	1.04354	1669.95	343.62	0.3813
0.54942	1.04135	1651.15	352.23	0.3860
0.59785	1.03992	1633.64	360.32	0.3904
0.64895	1.03765	1621.03	366.75	0.3939
0.69983	1.03576	1610.25	372.35	0.3969
0.78930	1.03274	1587.68	384.13	0.4031
0.81992	1.03182	1574.40	390.99	0.4067
0.83332	1.03101	1568.32	394.34	0.4084
0.88257	1.03054	1563.85	396.78	0.4097
0.89763	1.02993	1558.43	399.78	0.4113
0.95525	1.02892	1552.20	403.39	0.4131
1.00000	1.02823	1531.45	414.67	0.4188

water molecules. The addition of amide causes breaking of the hydrogen bonds between water molecules and formation of strong hydrogen bonds between the unlike molecules of the components. The first effect causes increase while the second decrease in  $\kappa_s$  and  $L_f$ . In the water rich region before minimum in  $\kappa_s$  and  $L_f$  is reached, the second factor overcomes, resulting in the decreasing of  $\kappa_s$  while in the amide rich region, after the minimum is occurred, the effect of the two factors is reversed and the compressibility starts increasing. In the case of FA/W mixture, the monotonic decrease of compressibility over the whole range of mole fraction is a result of their molecular chemical structure. Both FA and water molecules have the ability of forming hydrogen bonds affecting to a continuous transition from water molecules packing to an intermediate ordered packing of FA and water molecules and finally to pure FA and therefore to a monotonic decrease of  $\kappa_s$ .

An interesting remark on our experimental data concerning the pure components is that isentropic compressibility increases in the order:  $\text{PYR} < \text{FA} < \text{NMP} < \text{DMF} < \text{DMA}$  (table 7). The resulting conclusion is that the bisubstituted amides DMA, DMF are more compressible and therefore less rigid than monosubstituted (NMF) and unsubstituted (FA) amides, while the cyclic amides NMP and PYR are more rigid than their respective alkylated amides, suggesting that the compressibility decreases as more  $-\text{CH}_3$  groups are included in a molecule as it is pointed out [25] by Ali and Nain between NMF, DMF and DMA, and that the cyclic part of the amide molecules resists more than the alkyl part in compression as it is shown in the present investigation.

Unlike, the sequence of compressibility minima as well as intermolecular free length in (amide + water) mixtures is increased in the order:  $\text{PYR} < \text{NMP} < \text{DMA} < \text{DMF} < \text{NMF}$  (figure 1). The presence of water molecules causes a drastic change in compressibility, as a result of breaking the hydrogen bonding or dipole–dipole interactions as in the case of DMF, DMA, NMP, and consequent decrease of compressibility of amides, which is less in cyclic (amide + water) mixtures (PYR/W, NMP/W) and thereafter

TABLE 4  
Molar heat capacities at constant pressure  $C_p/(J^1 \cdot K^{-1} \cdot mol^{-1})$  of water and pure amides at 298.15 K

W	FA	NMF	DMF	DMA	PYR	NMP
75.292 <sup>a</sup> [38]	107.91 <sup>a</sup> , [48], [47] <sup>b</sup>	125.15 <sup>a</sup> [48] <sup>b</sup>	148.2 <sup>a</sup> [8]	178.2 <sup>a</sup> [1]	169.37 <sup>a</sup> [47] <sup>b</sup>	161.5 <sup>a</sup> [17] <sup>b</sup>
75.3 [8]	107.9 [1]	125.2 [36]	148.8 [49] <sup>b</sup>	175.98 [47] <sup>b</sup>		173.74 [50] <sup>b</sup>
75.01 [47] <sup>b</sup>	107.8 [19]	124.05 [47] <sup>b</sup>	150.57 [47] <sup>b</sup>			
		125.1 [20]	148.06 [37]			
			150.8 [20,36]			

<sup>a</sup> Used in this work.

<sup>b</sup> Computed from values in  $J^1 \cdot K^{-1} \cdot g^{-1}$  or  $cal^1 \cdot K^{-1} \cdot mol^{-1}$ .

TABLE 5  
Thermal expansibilities at constant pressure of water and pure amides  $\alpha_p/(10^{-3} \cdot K^{-1})$  at 298.15 K

W	FA	NMF	DMF	DMA	PYR	NMP
0.25705 [34]	0.768 <sup>a</sup>	0.905 <sup>a</sup>	1.010 <sup>a</sup>	1.001 <sup>a</sup>	0.788 <sup>a</sup>	0.864 <sup>a</sup>
	0.756 [35] <sup>b</sup>	0.873 [6] <sup>b</sup>	0.975 [10] <sup>b</sup>	0.960 [11]	0.726 [15] <sup>b</sup>	0.889 [52] <sup>b</sup>
			0.962 [24] <sup>b</sup>		0.817 [16] <sup>b</sup>	0.949 [53] <sup>b</sup>
			1.031 [51] <sup>b</sup>			0.912 [54] <sup>b</sup>

<sup>a</sup> Used in this work.

<sup>b</sup> Computed from data of the respective reference.

TABLE 6  
Densities and ultrasonic velocities of pure amides at various temperatures

T	FA	NMF	DMF	DMA	PYR <sup>a</sup>	NMP
			$\rho/(g \cdot cm^{-3})$			
288.15	1.13734	1.00785	0.95354	0.94558		1.03780
293.15	1.13267	1.00354	0.94912	0.94155		1.03323
296.15	1.12994	1.00081	0.94576	0.93783	1.10913	1.02963
298.15	1.12878	0.99911	0.94394	0.93634	1.10697	1.02823
300.15	1.12648	0.99731	0.94169	0.93436	1.10587	1.02610
303.15	1.12436	0.99446	0.93934	0.93166	1.10337	1.02451
308.15	1.11984	0.98977	0.93464	0.92704	1.09863	1.01993
			$u/(m \cdot s^{-1})$			
288.15	1618.36	1462.55	1496.60	1496.80		1587.94
293.15	1608.31	1447.15	1478.62	1478.98		1565.50
296.15	1602.08	1437.84	1465.00	1463.82	1640.44	1552.67
298.15	1597.79	1431.21	1457.49	1455.91	1633.95	1546.06
300.15	1593.83	1425.43	1449.24	1447.56	1627.16	1537.06
303.15	1587.14	1415.93	1438.32	1435.55	1617.61	1527.21
308.15	1576.40	1400.71	1418.95	1417.13	1601.87	1507.38

<sup>a</sup> Values of density and ultrasonic velocity in PYR are obtained above 296.15 as it is solid at lower temperatures.

in DMA/W, DMF/W and finally in NMF/W, where it has the higher value between the studied amides at the minimum position. However, the drop of the compressibility from pure amides ( $\kappa_{s,2}^*$ ) to their aqueous mixtures at the minimum position shows the following per cent decrease %  $(\kappa_s - \kappa_{s,2}^*)/\kappa_{s,2}^*$ : PYR/W (−10%), NMF/W (−22%), NMP/W (−24%), DMF/W (−29%) DMA/W (−35%). A maximum is also observed in relative association  $R_A$  (figure 2). The sequence of decreasing values of  $R_A$  at the maximum is the same as that of  $\kappa_s$ .

Finally, in figure 3 are shown the plots of  $\kappa_\phi$  vs.  $x_2$ . The sequence of the curves in the amide rich region follows the order: bisubstituted (DMA, NMP, DMF), monosubstituted (NMF, PYR) and unsubstituted (FA). In the water rich region,  $\kappa_{\phi,0}$  are calculated by interpolation of  $\kappa_\phi = f(x_2)$  plots and reflect the solute–solvent interactions

in the very dilute solutions. The values of  $\kappa_{\phi,0}$  expressed in  $10^3 cm^3 TP a^{-1} \cdot mol^{-1}$  are: FA  $5.4 \pm 0.1$ , NMF  $8.6 \pm 0.2$ , DMF  $7.1 \pm 0.1$ , PYR  $4.5 \pm 0.3$ . In contrary,  $\kappa_\phi$  in very dilute solutions of DMA and NMP (DMA in  $x_2 < 0.05$ , NMP in  $x_2 < 0.1$ ) shows a behavior fitted to the hydrophobic character of the dialkylated DMA and even more to the disubstituted NMP possessing the lactamic group.

The behavior of all (amide + water) mixtures deviate widely from the ideal mixing law as it is seen from plots of excess quantities  $u^E$ ,  $\kappa_s^E$ , and  $V^E$  vs.  $x_2$  (figures 4a, 5a, and 6, respectively). Excess molar volumes were calculated from our densities measurements although  $V^E$  are referred in the literature for a realistic anticipation with our ultrasonic properties where density is included in their computation. Our plots of  $V^E$  vs.  $x_2$  are in good coincidence with the

TABLE 7

Excess functions  $V^E$ ,  $\kappa_s^E$ ,  $u^E$ ,  $L_F^E$ , of binary mixtures of FA, NMF, DMF, DMA, PYR, NMP with water versus amide mole fraction  $x_2$  at 298.15 K

$x_2$	$V^E/(\text{cm}^3 \cdot \text{mol}^{-1})$	$\kappa_s^E/(\text{TPa}^{-1})$	$u^E/(\text{m} \cdot \text{s}^{-1})$	$L_F^E/(\text{Å})$
<i>Formamide</i>				
0.00000	0.0000	0.00	0.00	0.000
0.01258	-0.0175	-6.22	9.84	-0.003
0.01991	-0.0268	-9.41	15.00	-0.005
0.03610	-0.0448	-15.57	25.23	-0.008
0.05028	-0.0590	-20.10	32.99	-0.010
0.06473	-0.0721	-24.03	39.91	-0.012
0.07977	-0.0842	-27.49	46.18	-0.014
0.09437	-0.0947	-30.32	51.46	-0.015
0.11246	-0.1063	-33.23	57.07	-0.017
0.13468	-0.1181	-36.05	62.75	-0.018
0.15959	-0.1293	-38.37	67.71	-0.020
0.19461	-0.1394	-40.40	72.56	-0.021
0.22952	-0.1483	-41.46	75.60	-0.021
0.25478	-0.1528	-41.74	76.87	-0.022
0.27310	-0.1546	-41.67	77.28	-0.022
0.29195	-0.1559	-41.47	77.44	-0.022
0.33428	-0.1563	-40.46	76.67	-0.021
0.37110	-0.1542	-39.12	74.99	-0.021
0.40457	-0.1505	-37.62	72.84	-0.020
0.45522	-0.1441	-34.99	68.69	-0.019
0.48842	-0.1372	-33.08	65.52	-0.018
0.50252	-0.1345	-32.23	64.06	-0.017
0.52247	-0.1284	-30.99	61.95	-0.017
0.55641	-0.1224	-28.86	58.15	-0.015
0.59496	-0.1115	-26.35	53.61	-0.014
0.62975	-0.1031	-24.07	49.34	-0.013
0.67139	-0.0910	-21.28	44.07	-0.011
0.70199	-0.0827	-19.24	40.10	-0.010
0.72296	-0.0770	-17.82	37.30	-0.010
0.75440	-0.0664	-15.74	33.22	-0.009
0.77998	-0.0600	-14.06	29.81	-0.008
0.80943	-0.0508	-12.11	25.86	-0.007
0.83576	-0.0457	-10.39	22.27	-0.006
0.87518	-0.0333	-7.88	17.04	-0.004
0.91702	-0.0216	-5.23	11.42	-0.003
0.94653	-0.0168	-3.43	7.48	-0.002
0.97025	-0.0110	-2.00	4.36	-0.001
1.00000	0.0000	0.00	0.00	0.000
<i>N-Methylformamide</i>				
0.00000	0.0000	0.00	0.00	0.000
0.01572	-0.0371	-19.71	31.89	-0.010
0.03276	-0.0806	-37.87	61.69	-0.019
0.05095	-0.1261	-54.30	89.10	-0.027
0.07104	-0.1770	-69.47	114.63	-0.034
0.09226	-0.2243	-79.64	131.07	-0.039
0.11557	-0.2817	-89.52	146.92	-0.044
0.14098	-0.3343	-99.65	163.90	-0.049
0.17144	-0.3899	-106.83	174.95	-0.053
0.20054	-0.4394	-110.78	180.07	-0.055
0.23391	-0.4820	-112.91	181.90	-0.056
0.27138	-0.5223	-113.58	181.15	-0.056
0.30468	-0.5452	-113.04	178.94	-0.055
0.31855	-0.5525	-111.30	175.08	-0.054
0.33674	-0.5652	-109.20	170.42	-0.053
0.36149	-0.5675	-104.34	160.68	-0.051
0.38530	-0.5693	-98.39	149.15	-0.048
0.41658	-0.5555	-93.77	140.91	-0.045
0.44559	-0.5432	-88.76	132.10	-0.043
0.47853	-0.5318	-83.66	123.37	-0.040
0.51092	-0.5141	-78.71	115.21	-0.038
0.54968	-0.4916	-71.16	102.81	-0.034

TABLE 7 (continued)

$x_2$	$V^E/(\text{cm}^3 \cdot \text{mol}^{-1})$	$\kappa_s^E/(\text{TPa}^{-1})$	$u^E/(\text{m} \cdot \text{s}^{-1})$	$L_F^E/(\text{Å})$
0.58048	-0.4708	-66.12	94.87	-0.031
0.59133	-0.4525	-62.84	89.71	-0.030
0.61641	-0.4371	-58.84	83.53	-0.028
0.63352	-0.4139	-55.69	78.85	-0.026
0.68098	-0.3619	-46.20	64.58	-0.022
0.73228	-0.3110	-36.87	50.86	-0.017
0.77901	-0.2797	-31.09	42.58	-0.015
0.82792	-0.2284	-23.46	31.80	-0.011
0.85347	-0.1897	-18.92	25.50	-0.009
0.87627	-0.1481	-15.69	21.26	-0.007
0.91695	-0.1127	-10.31	13.75	-0.005
0.92850	-0.0958	-9.10	12.20	-0.004
1.00000	0.0000	0.00	0.00	0.000
<i>N,N-Dimethylformamide</i>				
0.00000	0.0000	0.00	0.00	0.000
0.01233	-0.0399	-25.50	41.69	-0.012
0.02660	-0.0938	-50.50	83.34	-0.025
0.04154	-0.1541	-72.49	120.67	-0.036
0.05803	-0.2256	-92.88	155.78	-0.046
0.07593	-0.3041	-110.41	186.03	-0.055
0.09542	-0.3892	-125.83	212.70	-0.062
0.11728	-0.4835	-137.31	231.26	-0.068
0.14116	-0.5796	-150.06	253.76	-0.075
0.16771	-0.6640	-158.58	267.87	-0.079
0.19751	-0.7584	-164.08	275.51	-0.081
0.23003	-0.8508	-166.89	277.88	-0.083
0.25288	-0.8743	-166.57	275.89	-0.082
0.28661	-0.9474	-164.42	268.79	-0.081
0.31385	-1.0129	-161.80	261.53	-0.079
0.37711	-1.0512	-151.05	238.51	-0.074
0.42474	-1.0810	-140.78	217.80	-0.068
0.44936	-1.0840	-135.43	207.65	-0.065
0.47547	-1.0882	-129.12	195.81	-0.062
0.49546	-1.0830	-122.71	183.91	-0.059
0.52028	-1.0867	-117.50	174.69	-0.056
0.53357	-1.0845	-113.43	167.39	-0.054
0.55499	-1.0692	-104.91	152.26	-0.050
0.58057	-1.0456	-99.69	143.92	-0.047
0.61685	-1.0296	-93.56	134.26	-0.044
0.63702	-0.9909	-87.23	124.06	-0.041
0.65512	-0.9485	-82.78	117.33	-0.039
0.69306	-0.8875	-75.83	107.10	-0.036
0.71724	-0.8430	-67.86	94.56	-0.032
0.73729	-0.8102	-61.54	84.77	-0.029
0.75301	-0.7750	-57.35	78.54	-0.027
0.76664	-0.7474	-54.76	74.88	-0.026
0.80367	-0.6458	-46.75	63.67	-0.022
0.81258	-0.6169	-44.03	59.75	-0.021
0.84695	-0.5363	-36.19	48.64	-0.017
0.86943	-0.4672	-33.27	45.06	-0.015
0.89110	-0.3933	-29.50	40.17	-0.014
0.92495	-0.2374	-18.78	25.50	-0.009
0.96614	-0.1522	-10.82	14.49	-0.005
1.00000	0.0000	0.00	0.00	0.000
<i>N,N-Dimethylacetamide</i>				
0.00000	0.0000	0.00	0.00	0.000
0.00083	-0.0032	-2.37	3.83	-0.001
0.00163	-0.0065	-4.60	7.44	-0.002
0.03959	-0.1995	-92.35	158.00	-0.046
0.05500	-0.2972	-114.46	197.41	-0.057
0.06456	-0.3566	-126.93	220.43	-0.063
0.08126	-0.4666	-140.68	243.58	-0.070

(continued on next page)

TABLE 7 (continued)

$x_2$	$V^E/(\text{cm}^3 \cdot \text{mol}^{-1})$	$\kappa_s^E/(\text{TPa}^{-1})$	$u^E/(\text{m} \cdot \text{s}^{-1})$	$L_f^E/(\text{Å})$
0.10004	-0.5895	-156.38	272.23	-0.078
0.12077	-0.7231	-169.46	295.82	-0.085
0.14474	-0.8664	-179.81	313.67	-0.090
0.17135	-1.0162	-187.00	324.76	-0.094
0.20119	-1.1582	-194.70	339.05	-0.098
0.23807	-1.3030	-191.45	325.91	-0.096
0.27612	-1.3764	-186.23	311.49	-0.092
0.32450	-1.4805	-179.41	294.43	-0.089
0.37834	-1.6074	-169.12	270.65	-0.083
0.41368	-1.6474	-161.87	255.57	-0.079
0.45195	-1.6634	-152.83	237.63	-0.074
0.48319	-1.6025	-143.45	220.24	-0.069
0.53716	-1.4855	-123.37	183.53	-0.059
0.58304	-1.3792	-110.23	161.48	-0.053
0.64962	-1.2004	-90.12	128.85	-0.043
0.70744	-0.9374	-70.76	99.40	-0.033
0.76331	-0.7875	-59.33	82.90	-0.028
0.83424	-0.6412	-34.06	44.63	-0.016
0.90531	-0.3116	-23.99	32.70	-0.011
1.00000	0.0000	0.00	0.00	0.000

*Pyrrolidin-2-one*

0.00000	0.0000	0.00	0.00	0.000
0.03793	-0.0476	-43.57	78.49	-0.022
0.05010	-0.0690	-53.07	97.70	-0.027
0.07966	-0.1264	-67.51	129.05	-0.035
0.10930	-0.1885	-81.75	163.16	-0.043
0.12204	-0.2101	-86.59	175.86	-0.046
0.15820	-0.2764	-92.62	193.94	-0.050
0.17894	-0.3250	-94.05	199.09	-0.051
0.21554	-0.3959	-94.45	203.25	-0.051
0.23523	-0.4532	-94.81	205.40	-0.052
0.24730	-0.4741	-94.82	206.56	-0.052
0.27938	-0.5141	-92.43	203.17	-0.051
0.34971	-0.5224	-84.65	189.56	-0.047
0.41989	-0.5098	-75.28	170.46	-0.042
0.50134	-0.4695	-63.76	145.62	-0.036
0.54904	-0.4374	-57.34	131.54	-0.032
0.61328	-0.4103	-48.80	112.15	-0.027
0.67049	-0.3517	-38.91	88.99	-0.022
0.70374	-0.3014	-34.66	79.64	-0.019
0.81170	-0.2425	-20.13	45.55	-0.011
0.83527	-0.2124	-17.34	39.24	-0.010
0.85927	-0.1834	-14.66	33.18	-0.008
0.88132	-0.1555	-12.04	27.23	-0.007
0.94126	-0.0801	-5.88	13.30	-0.003
1.00000	0.0000	0.00	0.00	0.000

*N-Methyl-2-pyrrolidinone*

0.00000	0.0000	0.00	0.00	0.000
0.02533	-0.0737	-53.37	75.66	-0.025
0.06006	-0.2095	-98.65	147.67	-0.048
0.08026	-0.3269	-119.31	184.60	-0.059
0.10081	-0.4307	-138.54	224.16	-0.069
0.11909	-0.5337	-143.31	230.03	-0.071
0.13994	-0.6502	-150.42	243.36	-0.075
0.15956	-0.7471	-152.43	245.13	-0.076
0.17789	-0.8124	-153.40	246.06	-0.077
0.19637	-0.8622	-154.26	247.87	-0.077
0.22033	-0.9214	-153.51	246.11	-0.077
0.23986	-0.9796	-152.83	244.85	-0.077
0.26016	-1.0415	-150.44	239.29	-0.075
0.27803	-1.0664	-148.26	235.24	-0.074
0.29867	-1.0931	-144.72	228.07	-0.073
0.32961	-1.1166	-139.03	217.20	-0.070

TABLE 7 (continued)

$x_2$	$V^E/(\text{cm}^3 \cdot \text{mol}^{-1})$	$\kappa_s^E/(\text{TPa}^{-1})$	$u^E/(\text{m} \cdot \text{s}^{-1})$	$L_f^E/(\text{Å})$
0.37937	-1.1359	-128.63	197.73	-0.064
0.44973	-1.1190	-114.82	174.61	-0.057
0.49861	-1.1092	-103.92	155.76	-0.052
0.54942	-1.0140	-91.51	135.21	-0.045
0.59785	-0.9478	-79.87	116.03	-0.039
0.64895	-0.8164	-69.78	101.66	-0.034
0.69983	-0.6934	-60.65	89.13	-0.030
0.78930	-0.4640	-42.96	63.48	-0.021
0.81992	-0.3848	-34.17	49.15	-0.017
0.83332	-0.3159	-29.99	42.61	-0.015
0.88257	-0.2598	-24.56	36.44	-0.012
0.89763	-0.2020	-20.67	30.50	-0.010
0.95525	-0.0868	-13.75	22.29	-0.007
1.00000	0.0000	0.00	0.00	0.000

literature [5,7]. The  $u^E$  has positive values while  $\kappa_s^E$ ,  $L_f^E$  and  $V^E$  negative. The negative deviations of  $\kappa_s^E$  and  $L_f^E$  curves reflect the existence of dipole–dipole or dipole-induced interactions or electron donor–acceptor complex formation. More negative values suggest stronger interactions between the unlike molecules and therefore less compressible structures. The deviations of bisubstituted amides (DMA, NMP, DMF) are greater in absolute values than monosubstituted (NMF, PYR) and these than unsubstituted (FA). This is in agreement with the conclusion of Garcia and all [5] from volumetric and viscosimetric results, where this behavior is attributed to more compact structures. Comparison of volumetric with ultrasonic behavior brings out a partial reversion of the sequence of amides curves and especially at the extremum position. The order of decreasing values of  $V^E$ ,  $\kappa_s^E$ , and increasing values of  $u^E$  is

$$\begin{aligned} V^E: & \text{FA} > \text{PYR} > \text{NMF} > \text{DMF} > \text{NMP} > \text{DMA} \\ \kappa_s^E: & \text{FA} > \text{PYR} > \text{NMF} > \text{NMP} > \text{DMF} > \text{DMA} \\ u^E: & \text{FA} < \text{NMF} < \text{PYR} < \text{NMP} < \text{DMF} < \text{DMA} \end{aligned}$$

The sequence of  $V^E$  curves (figure 6) is quite the same with that of  $\kappa_s^E$  (figure 5a) suggesting the same contribution of factors influencing these properties although we can notice some differences. FA and DMA keep the extremum positions in both sequences of  $V^E$  and  $\kappa_s^E$  while NMP and DMF interchange position. The sequence of curves  $L_f^E$  coincide with that of  $\kappa_s^E$ .

Comparing the extrema position of  $V^E$  vs.  $x_2$  with those of  $u^E$ ,  $\kappa_s^E$  and  $L_f^E$  vs.  $x_2$  we observe a considerable difference in  $x_2$  between the volumetric and ultrasonic properties. The mole fractions  $x_2(V^E)$  and  $x_2(\kappa_s^E)$  where minima of  $V^E$  and  $\kappa_s^E$  occur are given in table 9 as well as their relative difference  $[x_2(V^E) - x_2(\kappa_s^E)]/x_2(V^E)$ .

The  $[x_2(V^E) - x_2(\kappa_s^E)]/x_2(V^E)$  values reveal the influence of amide structure and amide–water interactions in the shifting of mole fraction where minima in  $V^E$  are observed to lower values in ultrasonic properties. This shifting is progressively increasing from primary FA ( $\approx 0.24$ ) to sec-



TABLE 8  
Coefficients  $A_i$  of Redlich–Kister equation and standard deviations  $\sigma(Y^E)$  of the binary (water + amides) mixtures at 298.15 K

$Y^E$	$A_0$	$A_1$	$A_2$	$A_3$	$A_4$	$\sigma(Y^E)$
<i>Formamide</i>						
$V^E/(\text{cm}^3 \cdot \text{mol}^{-1})$	-0.5399	-0.4175	-0.1408	-0.1123	-0.1798	0.0008
$u^E/(\text{m} \cdot \text{s}^{-1})$	257.77	200.69	121.89	116.07	93.52	0.25
$\kappa_s^E/(\text{TPa}^{-1})$	-164.31	-40.02	-14.44	-11.78	-9.93	0.04
$L_T^E/(\text{\AA})$	-0.069	-0.059	-0.037	-0.042	-0.035	0.015
<i>N-Methylformamide</i>						
$V^E/(\text{cm}^3 \cdot \text{mol}^{-1})$	-2.0890	-1.2535	-0.3679	0.7389	0.5711	0.0052
$u^E/(\text{m} \cdot \text{s}^{-1})$	470.16	629.87	558.55	339.55	94.89	2.11
$\kappa_s^E/(\text{TPa}^{-1})$	-454.77	39.74	79.52	-69.31	-48.62	1.02
$L_T^E/(\text{\AA})$	-0.154	-0.187	-0.146	-0.096	-0.043	0.001
<i>N,N-Dimethylformamide</i>						
$V^E/(\text{cm}^3 \cdot \text{mol}^{-1})$	-4.3526	-0.6150	-0.7882	0.3545	1.5384	0.0130
$u^E/(\text{m} \cdot \text{s}^{-1})$	732.79	892.13	761.31	588.96	458.49	2.27
$\kappa_s^E/(\text{TPa}^{-1})$	-653.50	193.78	-13.23	7.68	-103.70	1.52
$L_T^E/(\text{\AA})$	-0.235	-0.248	-0.191	-0.175	-0.162	0.001
<i>N,N-Dimethylacetamide</i>						
$V^E/(\text{cm}^3 \cdot \text{mol}^{-1})$	-6.2428	-3.2253	1.8031	2.59	-0.4495	0.0321
$u^E/(\text{m} \cdot \text{s}^{-1})$	837.62	1043.56	659.92	1003.64	1137.31	4.46
$\kappa_s^E/(\text{TPa}^{-1})$	-737.98	275.35	-212.55	-16.62	99.74	2.12
$L_T^E/(\text{\AA})$	-0.267	-0.292	-0.137	-0.280	-0.375	0.001
<i>Pyrrolidin-2-one</i>						
$V^E/(\text{cm}^3 \cdot \text{mol}^{-1})$	-1.9036	-1.3915	-0.7996	1.8690	1.8253	0.0128
$u^E/(\text{m} \cdot \text{s}^{-1})$	586.64	637.39	480.23	449.42	232.27	1.89
$\kappa_s^E/(\text{TPa}^{-1})$	-378.71	59.68	-12.54	-22.83	2.74	0.88
$L_T^E/(\text{\AA})$	-0.129	-0.147	-0.149	-0.148	-0.038	0.001
<i>N-Methyl-2-pyrrolidinone</i>						
$V^E/(\text{cm}^3 \cdot \text{mol}^{-1})$	-4.3222	-2.6520	-0.2270	1.3672	2.3956	0.0233
$u^E/(\text{m} \cdot \text{s}^{-1})$	257.77	200.69	121.89	116.07	93.52	0.06
$\kappa_s^E/(\text{TPa}^{-1})$	-611.31	147.59	-6.00	113.35	-113.11	1.72
$L_T^E/(\text{\AA})$	-0.205	-0.216	-0.171	-0.260	-0.274	0.001

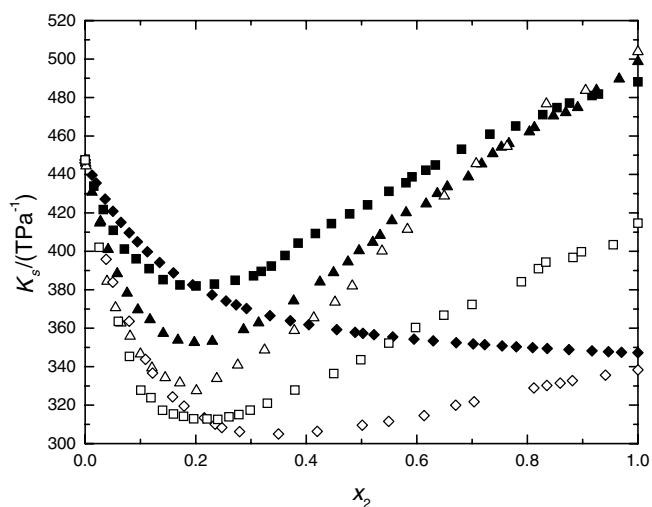


FIGURE 1. Isentropic compressibilities against the amide mole fraction: FA (◆), NMF (■), DMF (▲), DMA (△), PYR (◇), NMP (□) at 298.15 K.

ondary amides, NMF and PYR ( $\approx 0.30$ ) and thereafter to tertiary amides NMP, DMF, DMA ( $\approx 0.48, 0.52, 0.56$ ). Comparison of  $[x_2(V^E) - x_2(\kappa_s^E)]/x_2(V^E)$  with the  $\kappa_s^E/\kappa_s$  at the minimum (table 9) demonstrates that as more strong

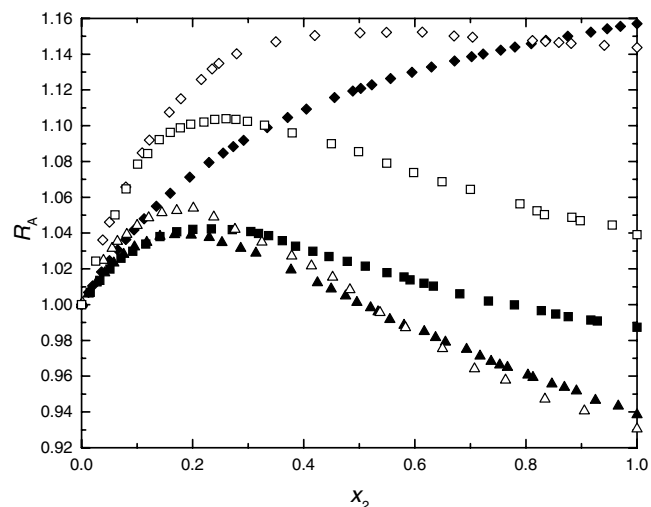


FIGURE 2. Relative association against the amide mole fraction: FA (◆), NMF (■), DMF (▲), DMA (△), PYR (◇), NMP (□) at 298.15 K.

are the interactions between amide and water molecules as greater is the shifting of mole fraction to lower values. Accordingly the sequence of interaction strength is FA < PYR < NMF < NMP < DMF < DMA. The mole fractions where minima in  $\kappa_s^E$  occur are in good coincidence

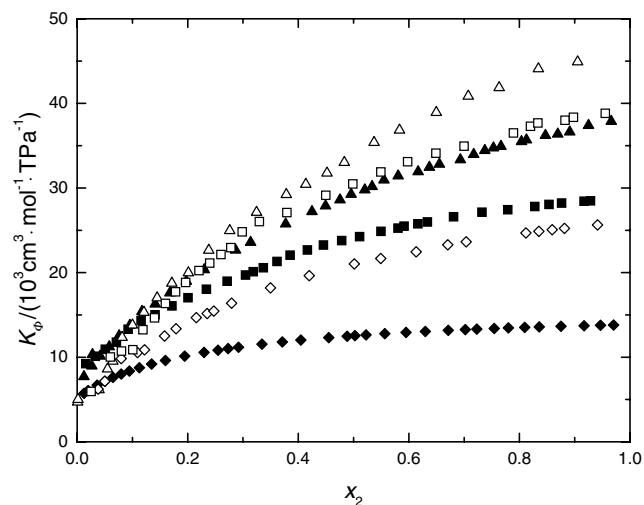


FIGURE 3. Apparent molar compressibilities against the amide mole fraction: FA (◆), NMF (■), DMF (▲), DMA (△), PYR (◇), NMP (□) at 298.15 K.

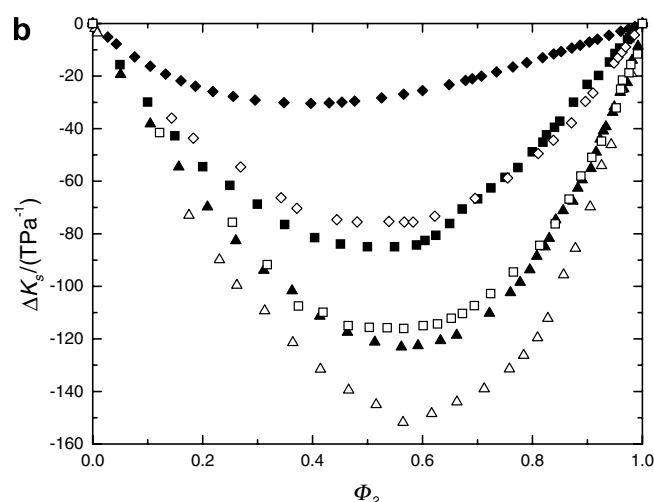
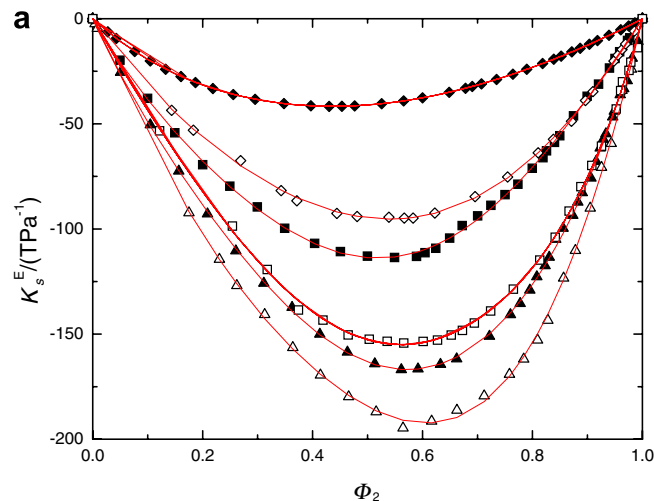


FIGURE 5. (a)  $\kappa_s^E$  and (b)  $\Delta \kappa_s$  against the amide ideal volume fraction: FA (◆), NMF (■), DMF (▲), DMA (△), PYR (◇), NMP (□) at 298.15 K. The points represent experimental values and the solid curves represent the smoothed values calculated from coefficients of equation (12).

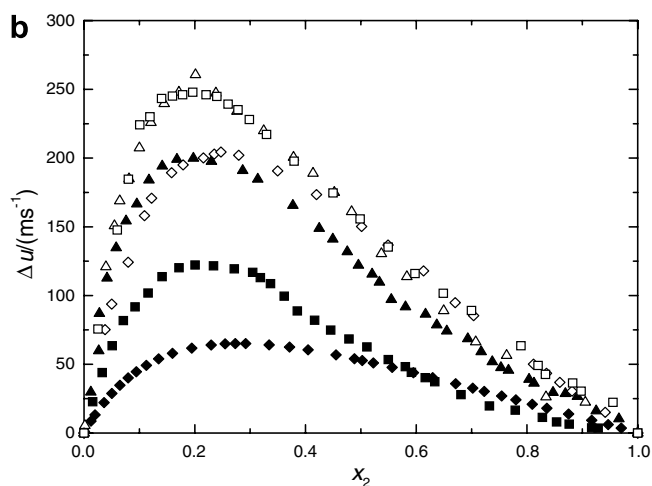
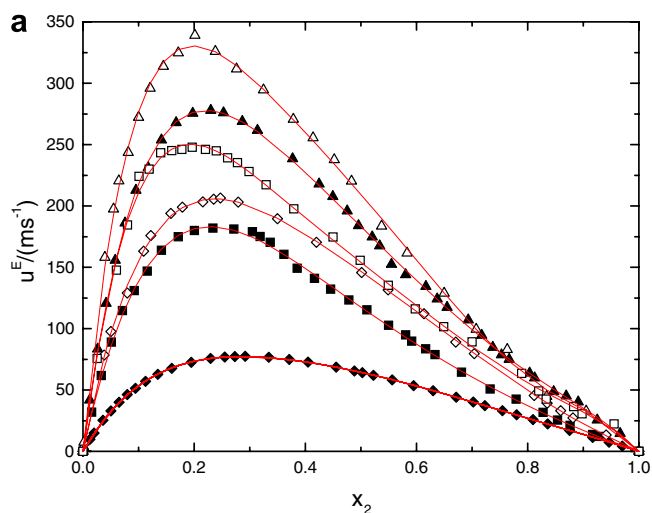


FIGURE 4. (a)  $u^E$  and (b)  $\Delta u$  against the amide mole fraction: FA (◆), NMF (■), DMF (▲), DMA (△), PYR (◇), NMP (□) at 298.15 K. The points represent experimental values and the solid curves represent the smoothed values calculated from coefficients of equation (12).

with literature values. In FA, a minimum in  $\kappa_s^E$  is observed [19] at  $x_2 \approx 0.27$ , in NMF [20] at  $x_2 \approx 0.17$ – $0.30$ , and in DMF [20]  $x_2 \approx 0.24$ . Several approaches have been proposed to elucidate the origin of the volumetric [13,57,58] and ultrasonic behavior [23,24,55,56,59] of solvents mixtures. This behavior may be influenced by (i) the breaking of the solvents molecular network which results in  $V^E$  and  $\kappa_s^E$  increase, and (ii) the interactions (dipole–dipole, dipole induced interactions, electron donor–acceptor complex formation or hydrogen bonds) between the (amide + water) molecules which results in  $V^E$  and  $\kappa_s^E$  decrease. A main also factor affecting this behavior are the geometrical effects allowing for the accommodation of molecules of different size into the cavities of molecular network. When the molecular sizes of the two solvents are quite different, the smaller molecules interpenetrate into the molecular network of larger molecules forming more rigid structures and consequently negative  $V^E$  and  $\kappa_s^E$  are observed. As the molecular sizes become equals, mixing results in a less

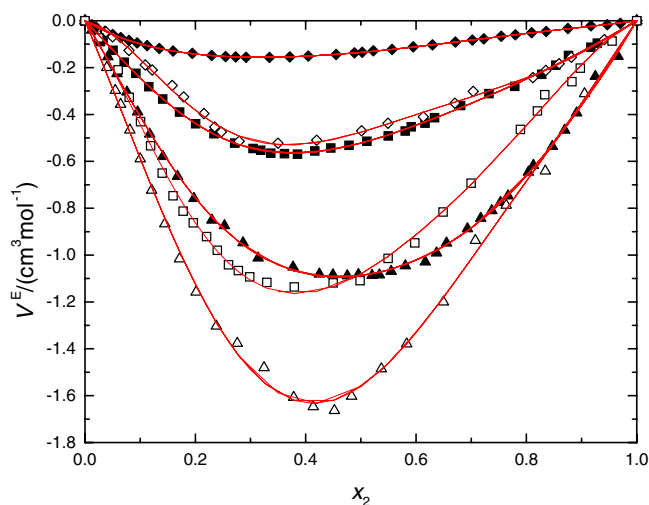


FIGURE 6.  $V^E$  against the amide mole fraction: FA (◆), NMF (■), DMF (▲), DMA (△), PYR (◇), NMP (□) at 298.15 K. The points represent experimental values and the solid curves represent the smoothed values calculated from coefficients of equation (12).

TABLE 9

Values of amide mole fractions  $x_2(V^E)$ ,  $x_2(\kappa_s^E)$ , their relative differences  $[x_2(V^E) - x_2(\kappa_s^E)]/x_2(V^E)$  and the ratios  $\kappa_s^E/\kappa_s$ ,  $\Delta\kappa_s/\kappa_s$  at the extremum position

	$x_2(V^E)$	$x_2(\kappa_s^E)$	$[x_2(V^E) - x_2(\kappa_s^E)]/x_2(V^E)$	$\kappa_s^E/\kappa_s$	$\Delta\kappa_s/\kappa_s$
FA/W	0.334	0.255	0.236		
NMF/W	0.385	0.271	0.296	-0.295	-0.221
DMF/W	0.475	0.230	0.516	-0.472	-0.348
DMA/W	0.452	0.201	0.555	-0.594	-0.463
PYR/W	0.350	0.247	0.296	-0.308	-0.245
NMP/W	0.379	0.196	0.483	-0.493	-0.371

well packed structure, and positive  $V^E$  and  $\kappa_s^E$  are observed [59]. These trends are observed in our investigation. In DMA/W solution, possessing the larger molecule between the amides studied and a strong proton-accepting ability, the two negative factors dominate and the greater deviations are observed. As the amide molecule becomes smaller (as in FA mixture), hydrogen bonding is less strong and the ability of molecule's accommodation is limited. The result of the two opposite factors is the decrease of  $V^E$  and  $\kappa_s^E$ . The minima shifting to lower values could reflect the different origin of the response of these properties to the formed structures at the extrema. A discrepancy in extrema position is showed also between ultrasonic properties and excess dielectric constants of (amide + water) mixtures [26].

As it concerns the evaluation of excess quantities [28,29], the results demonstrate clearly that the use of approximated deviation of ideality  $\Delta Y$  instead of  $Y^E$  leads to quite different estimations concerning the magnitude of interactions between unlike molecules which could be critical especially when we are interested in a comparative investigation. The plots of the differences  $\Delta u$ , and  $\Delta\kappa_s$  due to the mixing of pure components are shown in figure 4b and 5b, respectively. In this study the deviation from ideality is investigated by the quantities  $u^E$ , and  $\kappa_s^E$  calculated by

thermodynamically derived equations (5)–(8) and the  $\Delta u$ , and  $\Delta\kappa_s$  computed by the most frequently used equation (10). The comparison is very revealing (table 9). The values of properties at extrema are significantly different and in some cases the sequence is changed, as it is shown in figure 4. between  $u^E$  and  $\Delta u$ .

We notice that the two different approaches in computation of deviations imply different estimations concerning the strength of molecular interactions between (amide + water) molecules. They also point out the importance of use of the convenient approximation especially for comparative reason. Comparing the magnitude of deviations (not only the sequence of minima) between the two approaches we found that the ratios  $\kappa_s^E/\kappa_s$  and  $\Delta\kappa_s/\kappa_s$  of the extremum values of  $\kappa_s^E$ ,  $\Delta\kappa_s$  and  $\kappa_s$  differ significantly (table 9) while the strength of interactions in both cases follows the order: FA < PYR < NMF < NMP < DMF < DMA.

#### 4. Conclusions

The ultrasonic properties in (amide + water) mixtures exhibit a maximum in ultrasonic velocity and relative association and a minimum in isentropic compressibility and intermolecular free length *vs.*  $x_2$  except in the case of FA/W where they change monotonically. The sequence of compressibility minima is increased in the order PYR < NMP < DMA < DMF < NMF revealing that compressibility in the cyclic (amide + water) mixtures is less than in dialkylated and these than the monoalkylated amides. The behavior of all (amide + water) mixtures deviate widely from ideal mixing law as it is expressed by the excess ultrasonic properties  $u^E$ ,  $\kappa_s^E$ . The magnitude of deviations and the sequence of superimposed curves reflect the strength of interactions between the unlike molecules. The more negative values suggest stronger interactions between the unlike molecules and therefore less compressible structure. The decreasing order of  $\kappa_s^E$  is FA < PYR < NMF < NMP < DMF < DMA. Comparison of ultrasonic with volumetric properties reveals a shifting of the mole fractions of amide at the extrema positions to lower values which is related with the strength of intermolecular interactions. The reduced difference  $[x_2(V^E) - x_2(\kappa_s^E)]/x_2(V^E)$  in position, reveals the influence of the amide structure and (amide + water) interactions and it is progressively increased from unsubstituted (FA) to monosubstituted (NMF, PYR) and thereafter to bisubstituted (NMP, DMF, DMA) amides in accordance with the magnitude of excess molar compressibility deviations. Finally, the two approaches used in calculating deviations of excess ultrasonic properties from ideality and therefore the magnitude of interactions could lead to different estimations of the strength of intermolecular interactions.

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