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CRYOSCOPIC AND DYNAMIC STUDY OF THE MOLTEN SYSTEM FLUOROACETAMIDE–SODIUM TRIFLUOROACETATE

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Abstract

The behavior of the molten system acetamide–electrolyte, including the peculiarity of the structure and the consequent relevant properties, such as the megavalue of the dielectric constant, was reported earlier. The probable structure is a micellar system composed of salt micelles dispersed in an amorphous solvent. The present paper reports measurements in a related system: fluoroacetamide–sodium trifluoroacetate. The phase diagram, the ultrasonic absorption of both longitudinal and shear waves, and the longitudinal relaxation time of the nuclear magnetic momentum were measured at different temperatures. The most important result was that T_1 (NMR relaxation time) on the ^{19}F nucleus shows that the amide and salt participate in different environments. The amide environment is less rigid; this proves that the system must be considered microheterogeneous. Moreover, the present system exhibited: 1) a less extended concentration area where supercooling phenomena occur; 2) a much broader curve of the real part of the mechanical impedance versus frequency; 3) a higher bulk viscosity in comparison with the CH_3CONH_2–CF_3COONa supercapacitive system.

Keywords: amide, bulk viscosity, micelle, NMR relaxation time, viscoelasticity

Introduction

Molten system composed of acetamide and salts such as NaSCN, CF_3COONa or $Ca(NO_3)_2$, display supercooling phenomena. The supercooled mixtures are microheterogeneous and exhibit very high dielectric constants [1, 2]. We have tried to explain this dielectric peculiarity on the basis of a heterogeneous model [3] of charged domains. The use of a fluorinated amide as solvent allows us to prove the microheterogeneous nature, through measurement of the NMR relaxation time (T_1) of the fluorine nucleus (proton decoupled) of both the salt and the amide, and also to examine the variation of viscoelastic and bulk properties in order to improve the knowledge of these microheterogeneous systems.

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Experimental

The cryoscopic method is described in previous papers [4, 5]. Ultrasonic, viscoelastic and NMR relaxation were studied by using the same methods as described previously [1, 2, 6]. Sodium trifluoroacetate from Ega was dried at 100°C under dynamic vacuum. Fluoroacetamide from Fluka was recrystallized from C_2H_5OH, dried under dynamic vacuum at 60°C, and then stored in a dry box. The relaxation study was performed on the solution with an amide mole fraction of 0.4766.

Results

Cryoscopy

Figure 1 depicts the liquid–solid equilibrium temperature *vs*. the mole fraction for the binary mixture CH_2FCONH_2–CF_3COONa. Supercooling phenomena were observed in the dashed mole fraction range.

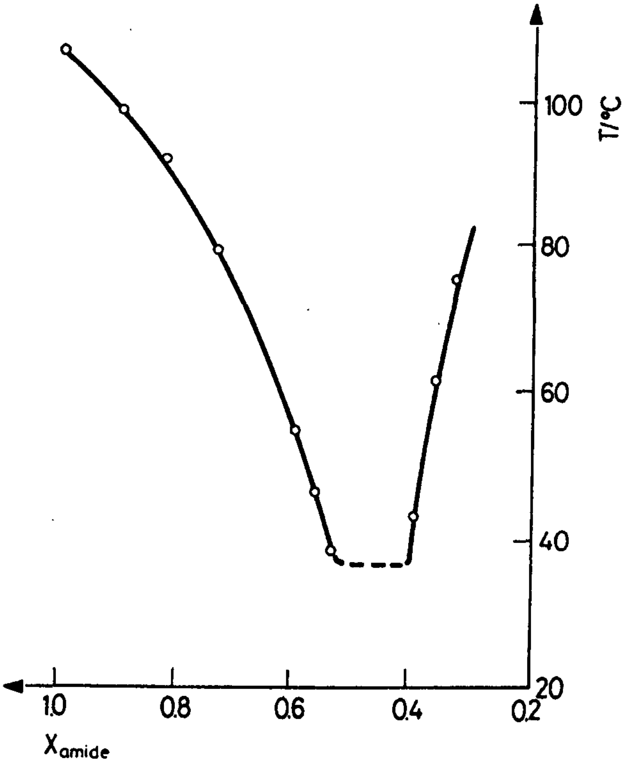

Fig. 1

NMR

T_1 (longitudinal relaxation time) was measured for the ^{19}F of CF_3COONa (singlet) and CH_2FCONH_2 (triplet). The results are given in Table 1.

Table 1 Longitudinal relaxation time (T_1) at different temperatures for the ^{19}F nuclei

T_1 /s		T / °C
^{19}F (singlet)	^{19}F (triplet)	
0.826	0.280	50
0.758	0.198	40
0.709	0.114	30

Viscoelasticity

With the normal incidence technique [7], the real part, R, of the mechanical impedance, Z, was measured, and a plot of $R/(\rho G_\infty)^{1/2}$ *vs.* $\omega\eta/G_\infty$ was obtained, using the variable superposition method employed previously [2, 4] (ρ and G_∞ being the density and the high-frequency rigidity modulus, respectively). This is shown in Fig. 2. The B.E.L. [8] parameters fitting the experimental measurements are K=13 and β=0.55.

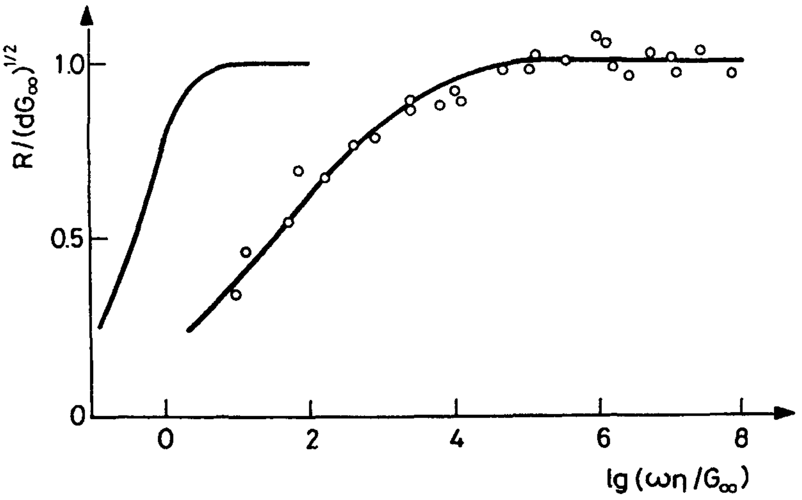

Fig. 2

Ultrasonics

The ultrasonic losses were measured at 20.5, 40.8 and 60.2°C and between 5 and 65 MHz. Viscosity, density and ultrasonic velocity (measured at 15 MHz)

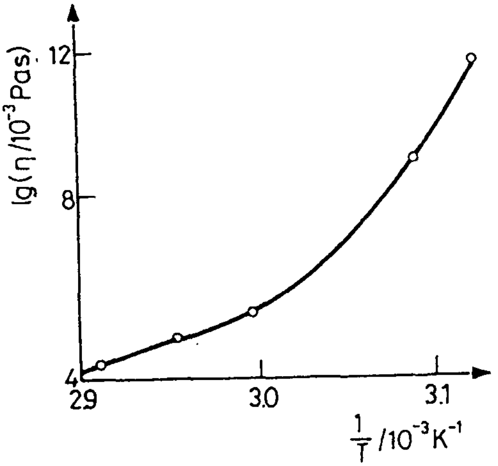

Fig. 3

were also measured as reported previously [2, 6] in order to calculate the classical absorption. Viscosity is shown in Fig. 3. Density data were fitted by means of the equation:

$$\frac{\rho}{\mathrm{kg\cdot m^{-3}}} = 1714.63 - 1.2403\,\frac{t}{^\circ\mathrm{C}} \tag{1}$$

The classical absorption is reported in Table 2.

Table 2 Calculation of classical absorption from density, viscosity and ultrasonic velocity

T / °C	ρ / kg·m^{-3}	η / Pa s	U / m s^{-1}	(α/f^2) / 10^{-9} s^{2}m^{-1}
20.5	1258:89	14086.9	3582.3	6.41
40.8	1246.84	53.5	2530.0	$6.97\cdot10^{-2}$
60.2	1235.31	0.49	2485.7	$6.79\cdot10^{-4}$

At 20.5 and 40.8°C, the calculated classical absorption greatly exceeds the experimental absorption, whereas at 60.2°C $(\alpha/f^2)_{\mathrm{exp}} > (\alpha/f^2)_{\mathrm{class}}$.

In this case, a plot of $[(\alpha/f^2)_{\mathrm{exp}} - (\alpha/f^2)_{\mathrm{class}}]^{-1}$ *vs.* the square frequency shows that one relaxation phenomenon is present and allows calculation of the relaxation frequency and bulk viscosity, which are shown in Table 3.

Table 3 Ultrasonic relaxation parameters

T / °C	f_r / MHz	η / Pa s
60.2	58	10.3
40.8	5.4	163.4

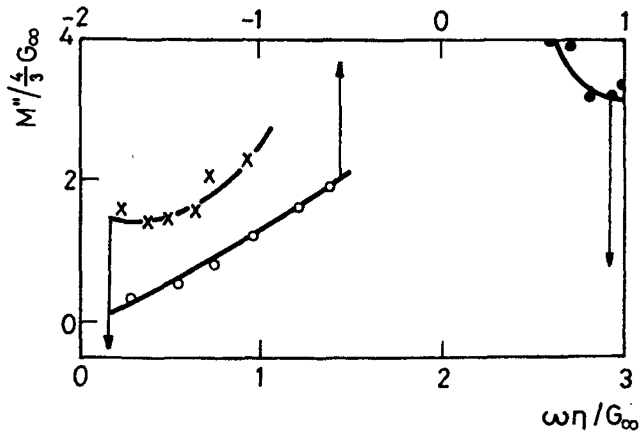

Fig. 4

At 40.8 and 20.5°C, the imaginary part, M'' of the complex longitudinal modulus is calculated from the measured absorption [9]. A plot of M'' *vs.* the reduced frequency is shown in Fig. 4. It is evident that two relaxation phenomena appear. Only at 40.8°C were we able to calculate the relaxation parameters of the faster phenomenon (given in Table 3). The calculation was performed by comparing, in a reduced plot, M''/G_∞ and G''/G_∞ (obtained from the B.E.L. model with $K=13$ and $\beta=0.55$). This allows calculation of the compressional modulus K'', whose trend *vs.* the frequency [9] gives the parameters shown in Table 3.

Discussion

When CH_3CONH_2 in the mixture is replaced by CH_2FCONH_2, several differences in experimental behaviour have been observed in comparison with the binary system CH_3CONH_2–CF_3COONa.

1) Supercooling phenomena occur in a very limited concentration range. In the binary system CH_3CONH_2–CF_3COONa, the supercooling area covers the range $0.31<X_{salt}<0.69$, as opposed to $0.48<X_{salt}<0.60$ for the present system;

2) the viscoelastic relaxation occurs in a very wide frequency range, showing a spread of relaxation times;

3) the bulk viscosity is much higher in the present mixture.

Obviously, a different structure is the basis of the observed behaviour.

NMR relaxation shows that the fluorine nucleus of the amide has a relaxation time, T_1, much lower than that of the fluorine nucleus of the salt. The relaxation is ensured by the fluctuation of the local magnetic field caused by the tumbling of the molecules [10] according to mechanisms such as DD or SR.

The experimental results suggest that the amide and salt molecules participate in different packages, and that the amide environment is less rigid than that of the salt molecule.

The microheterogeneous structure of the amide–salt mixtures was also presumed in the systems studied previously [11, 12]. The fact that in the present system the supercooled mixtures are less stable, showing a tendency to recrystallize in time, meant that we were not able to study the ultrasonic relaxation frequency as a function of the salt concentration. For this reason, we cannot identify the kinetic mechanism responsible for the relaxation. In the previous system, it was controlled in the stable mixtures and was attributed to an equilibrium of the amide between two states [2]. In any case, the present relaxation involves higher energy (Table 3), but the velocity of the phenomenon does not change appreciably; the ratio η_B/η is strongly dependent on temperature, as expected for non-structural relaxation. We can conclude that the introduction of a fluorine atom into the solvent molecule produces a change in the package of salt molecules, but the system again shows microheterogeneity, with amide domains and salt domains.

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Zusammenfassung — Bereits früher wurde über das Verhalten des geschmolzenen Systemes Acetamid-Elektrolyt, einschließlich der besonderen Konfiguration der Struktur und der darausfolgenden relevanten Eigenschaften, wie z.B. der besonders hohe Wert der Dielektrizitätskonstante, berichtet. Die wahrscheinliche Struktur ist ein Mizellensystem, bestehend aus Salzmizellen, die in einem amorphen Lösungsmittel dispergiert sind. Vorliegend werden Messungen an

einem verwandten System beschrieben: Fluoracetamid-Natriumtrifluoracetat. Bei verschiedenen Temperaturen wurde das Phasendiagramm, die Ultraschallabsorption sowohl für Longitudinal- als auch für Schubwellen und die longitudinale Relaxationszeit des Kernmagnetmomentes gemessen. Das wichtigste Ergebnis war, daß die *T1* (NMR Relaxationszeit) an den ^{19}F-Kernen zeigt, daß Amid und Salz in verschiedener Umgebung vorkommen. Die Amid-Umgebung ist weniger starr; dies zeigt, daß das System als mikroheterogen betrachtet werden muß. Weiterhin ergab das fragliche System: 1) einen weniger ausgedehnten Konzentrationsbereich, in dem Unterkühlungserscheinungen vorkommen; 2) eine breitere Kurve des reellen Teiles der mechanischen Impedanz in Abhängigkeit von der Frequenz; 3) eine größere Viskosität als das superkapazitive System CH_3CONH_2–CF_3COONa.