

## Density, viscosity and electrical conductivity of the binary mixture *N*-butylurea and CF<sub>3</sub>COONa (1.9206:1)

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(Received 24 February 1992)

### Abstract

Liquid–solid equilibrium temperatures of the *N*-butylurea and sodium trifluoroacetate molten binary system were measured in the concentration range allowed by the thermal stability of the amide. Although real supercooled phenomena do not appear, the liquid mixture of molar fraction  $X_1 = 0.6576$  remains in the liquid state at nearly 30°C so that the measurements of density, viscosity, and electrical conductivity may be performed.

### INTRODUCTION

For a few years now, we have been studying the behavior of the molten amides employed as electrolyte solvents [1–14]. In some cases the liquid mixtures show remarkable supercooling phenomena, mainly in those containing an Na<sup>+</sup> ion [3–6]. Moreover, these supercooled liquids exhibit viscoelastic behavior [15–18], high ultrasonic losses in the megahertz region [19] and dielectric relaxation [20]; all these peculiarities may be explained on the basis of a polymeric structure built via aggregation phenomena of solvated ions. In this paper we present the results of cryoscopic, densimetric, viscosimetric, and electrical conductimetric measurements for the binary system *N*-butylurea–CF<sub>3</sub>COONa.

### EXPERIMENTAL

The experimental method for the cryoscopy has been described previously [21]. Melting points near room temperature were measured using the equipment described by Braghetti et al. [22] refrigerated by a Haake F3 cryostat.

Density measurements were performed using a DM 55 vibrating precision densimeter (manufactured by Anton Paar K.G., Austria)

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calibrated with doubly distilled and deaerated water and air. Electrical conductivity was measured with a digital conductivity meter mod. 134 (manufactured by AMEL, Italy) and an AMEL conductivity cell 192 K1, checked by means of potassium chloride solutions. The cell constant was calculated using the mean values of the specific conductivity of KCl solutions given by Kohlrausch and Jones (see ref. 23). For both the density and the electrical conductivity, the temperature was controlled by means of a Heto (Denmark) thermocryostat. The Hoespler equipment described previously [24] was utilized for the viscosity measurements. The chemicals employed, without further purification, were KCl (Carlo Erba RPE),  $\text{CF}_3\text{COONa}$  (>98% Fluka) hot dried under dynamic vacuum and  $\text{CH}_3(\text{CH}_2)_3\text{NHCONH}_2$  (>99% Fluka) dried at room temperature for several days under dynamic vacuum. In this paper, 1 denotes *N*-butylurea and 2 denotes  $\text{CF}_3\text{COONa}$ .

## RESULTS AND DISCUSSION

Liquid–solid equilibrium temperatures, as a function of the mole fraction of *N*-butylurea, are given in Table 1. The plot of  $T/X_1$  of the liquid–solid boundary curve is presented in Fig. 1. Figure 2 shows the trend of  $\Delta T/(\nu mK)$  versus  $m$ , where  $\Delta T$  is the cryoscopic lowering,  $\nu$  the total number of ions in the salt formula,  $m$  the molality, and  $K$  the thermodynamic cryoscopic constant of *N*-butylurea ( $9.05 \text{ K kg mol}^{-1}$ ), deduced from the literature [25]. Figure 3 shows the trend of the mean ionic activity coefficient  $f$  of the sodium trifluoroacetate, evaluated using the Gibbs–Duhem relation, as a function of the molar fraction of the *N*-butylurea. Because the amide did not show high thermal stability, when in mixture with electrolytes, we investigated the concentration range up to

TABLE 1

Liquid–solid equilibrium temperatures in the binary system  $\text{CH}_3(\text{CH}_2)_3\text{NHCONH}_2$ – $\text{CF}_3\text{COONa}$

$X_1$	$T$ (K)	$X_1$	$T$ (K)
1.0000	370.1	0.8173	337.5
0.9883	368.0	0.7991	333.8
0.9755	366.6	0.7576	327.0
0.9664	365.3	0.7410	323.7
0.9544	362.8	0.7201	320.3
0.9449	360.0	0.6983	314.8
0.9314	358.7	0.6798	313.7
0.9130	355.4	0.6728	311.6
0.8983	351.4	0.6598	310.1
0.8774	347.8	0.6507	314.2
0.8472	341.9		

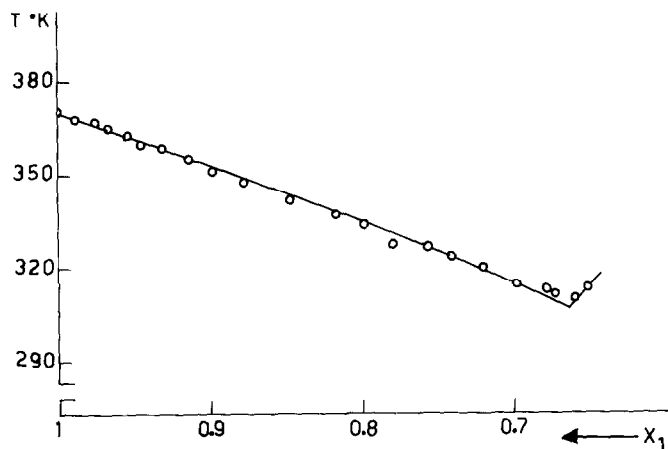


Fig. 1. Liquid-solid boundary curve for the binary system *N*-butylurea-sodium trifluoroacetate.

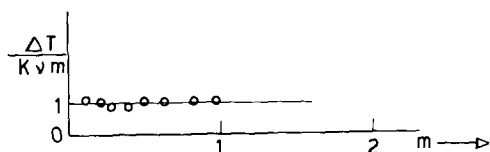


Fig. 2. Trend of  $\Delta T/(\nu Km)$  vs.  $m$ .

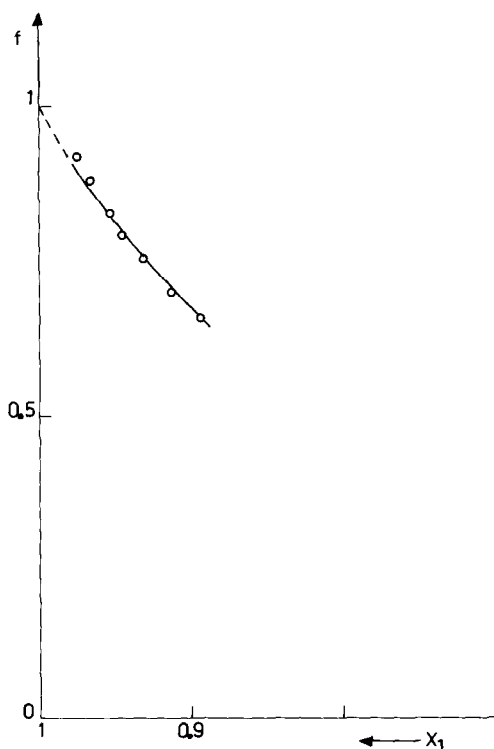


Fig. 3. Graphic trend of the mean ionic activity coefficient  $f$  as a function of the *N*-butylurea molar fraction.

the mole fraction  $X_1 = 0.6507$ . Density, viscosity and electrical conductivity measurements were performed between 29.1 and 50°C for the liquid mixture of mole fraction  $X_1 = 0.6576$ . Experimental density values  $\rho$ , fitting the equation

$$\rho = 1.48 - 0.89 \times 10^{-3}T$$

are given in Table 2, and the experimental results of viscosity  $\eta$ , and specific electrical conductivity  $\chi$ , are given in Tables 3 and 4 respectively. Figures 4 and 5 show the dependence of the viscosity  $\eta$ , and of the equivalent conductivity  $\Lambda$ , respectively, on  $T$  according to the Arrhenius plot.

The graphical trends shown in Figs. 2 and 3 demonstrate the following features.

(a) The electrolyte is completely dissociated at the investigated concentrations; therefore the substitution of the H atom with the butyl group,

TABLE 2

Density values  $\rho$  as a function of  $T$  for the mole fraction 0.6576

$T$ (K)	$\rho$ (g cm <sup>-3</sup> )	$T$ (K)	$\rho$ (g cm <sup>-3</sup> )
322.5	1.1962	308.5	1.2084
321.5	1.1971	307.4	1.2095
319.4	1.1987	306.4	1.2104
314.3	1.2031	305.4	1.2114
311.5	1.2056	303.3	1.2134

TABLE 3

Viscosity values  $\eta$  as a function of  $T$  for the mole fraction  $X_1 = 0.6576$

$T$ (K)	$\eta$ (cP)	$T$ (K)	$\eta$ (cP)
322.4	2.1	310.4	9.6
317.5	3.7	305.5	19.6
314.3	5.4	302.2	32.4
311.4	8.5		

TABLE 4

Specific electrical conductivity  $\chi$  as a function of  $T$  for the mole fraction  $X_1 = 0.6576$

$T$ (K)	$\chi$ ( $\times 10^3 \Omega^{-1} \text{cm}^{-1}$ )	$T$ (K)	$\chi$ ( $\times 10^3 \Omega^{-1} \text{cm}^{-1}$ )
323.2	46.4	318.2	28.5
321.8	40.1	314.2	18.6
321.2	38.4	310.3	11.8
319.2	31.6	308.3	9.3

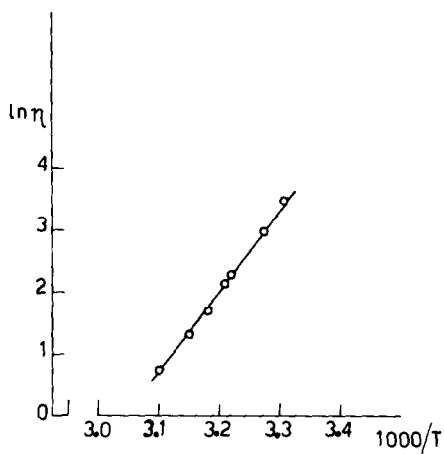


Fig. 4. A plot of  $\ln \eta$  versus  $1/T$  for the mole fraction  $X_1 = 0.6576$  ( $\eta$  in cP).

in the  $\text{NH}_2$  group of the urea, makes the amide a good solvent for the sodium trifluoroacetate.

(b) A comparison of these data with previously published data [13, 14] concerning different salts in urea shows that the solute–solvent interaction in this system is of the same order of the systems in urea.

The binary system reported in this paper does not generally show supercooling phenomena; only in the mole fraction range around  $X_1 = 0.6576$  do the mixtures crystallize with increasing difficulty when the

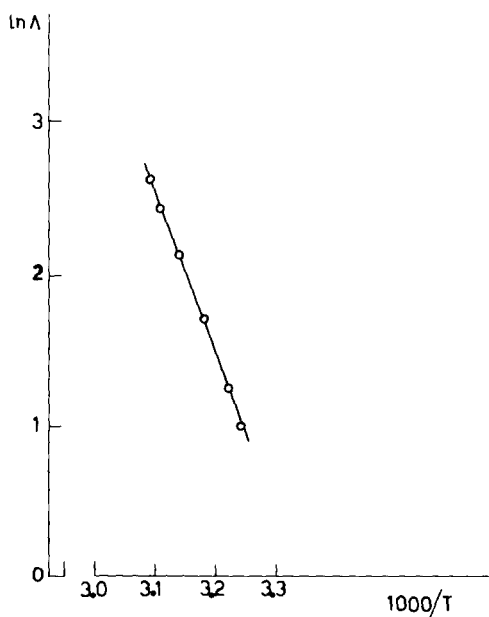


Fig. 5. A plot of  $\ln \Lambda$  versus  $1/T$  for the mole fraction  $X_1 = 0.6576$  ( $\Lambda$  in  $\Omega^{-1} \text{ cm}^2 \text{ eq}^{-1}$ ).

0.6576 mole fraction value is approached. The experimental results of the viscosity and electrical conductivity measurements suggest that the slope of the Arrhenius plots should be regarded as a temperature coefficient rather than a true activation energy  $E_{act}$ , owing to the equilibria present in the solution.

#### ACKNOWLEDGMENTS

We are grateful to the Ministero dell'Università e della Ricerca Scientifica e Tecnologica for financial support, and to R. Borgarucci for technical assistance.

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