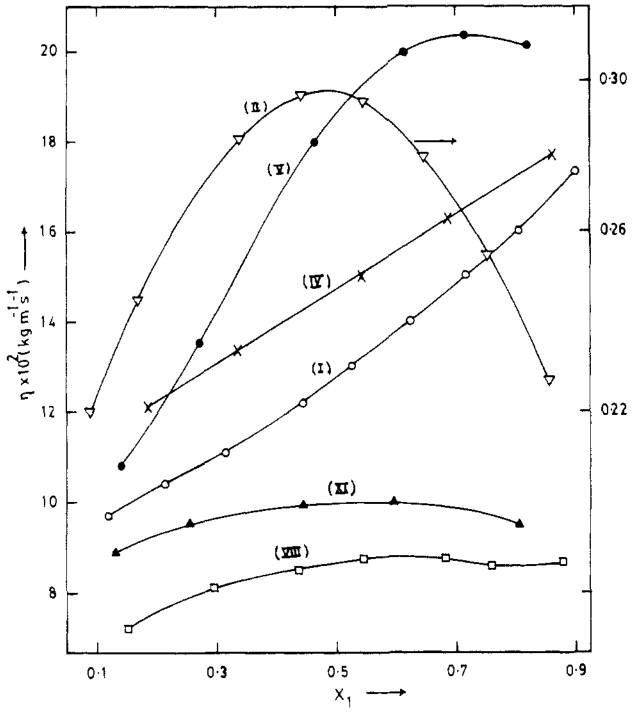

**Figure 1.** Viscosity vs. composition of the mixture. The numbers for the curves refer to systems mentioned in Table II.

ment. However, to our knowledge, no literature data on viscosities of binary mixtures containing bromoform were available and thus we could not compare the data with the literature findings.

## Acknowledgment

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**Registry No.** Benzene, 71-43-2; carbon tetrachloride, 56-23-5; cyclohexane, 110-82-7; bromoform, 75-25-2; methyl ethyl ketone, 78-93-3; dimethyl sulfoxide, 67-68-5; ethyl acetate, 141-78-6; methanol, 67-56-1; nitromethane, 75-52-5; dimethylformamide, 68-12-2; bromobenzene, 108-86-1; *p*-xylene, 106-42-3.

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# Solubility Curves of Some Electrolytes ($CF_3COONa$, $NaClO_4$, $KClO_4$) in Molten 1,3-Dioxolan-2-one

**Giancarlo Gioia Lobbia* and Gianfrancesco Berchiesi**

*Dipartimento Scienze Chimiche, Università di Camerino, 62032 Camerino, Italy*

**With the aim of investigating the interactions between an electrolyte and a nonaqueous solvent we present in this note the liquid-solid equilibria in the binary mixtures of 1,3-dioxolan-2-one (ethylene carbonate) and electrolytes.**

## Introduction

In previous papers (*1-8*) we showed that some amide solvents in mixtures with particular electrolytes (*3*) exhibit, with regard to crystallization, a peculiar behavior. The most probable explanation is the following: the presence of solutes stabilizes an open dimeric structure of the amide (*9*, *10*), which at low temperature (around the eutectic point) may polymerize giving these liquids a viscoelastic behavior in the ultrasonic frequency region (*11-13*).

Other liquids have been tested such as succinimide (*4*), but the crystallization behavior is not so anomalous as with low molecular weight amides. The behavior observed and the formation of polymeric structures are related (a) to the presence of cations (alkali or alkali earth) and anions derived from strong acids (*3*) and (b) probably to the possibility of hydrogen-bond formation (*4*). In order to check the latter point we investigated electrolyte solution behavior in $C_2H_4CO_3$, owing to the fact that this solvent cannot form hydrogen bonds.

## Experimental Section

The experimental cryoscopic technique is reported in a previous paper (*14*). The 1,3-dioxolan-2-one (ethylene carbonate) (Fluka) is employed without further purification and dried under dynamic vacuum at room temperature. The following chemicals were used: $NaClO_4$ and $KClO_4$ (Erba), KCNS (Merck), NaCNS, HCOONa, and $NaNO_3$ (Fluka), $CF_3COONa$ (Ega-Chemie). The purity of all the compounds employed was not less than 98%. These compounds were stored in a desiccator under dynamic vacuum.

## Results and Discussion

The following electrolytes were employed as solutes: $NaNO_3$, HCOONa, NaCNS, KCNS, $CF_3COONa$, $KClO_4$, $NaClO_4$. Sodium nitrate, sodium formate, sodium thiocyanate, and potassium thiocyanate practically do not dissolve in ethylene carbonate. The others are soluble, and it was possible to measure liquid-

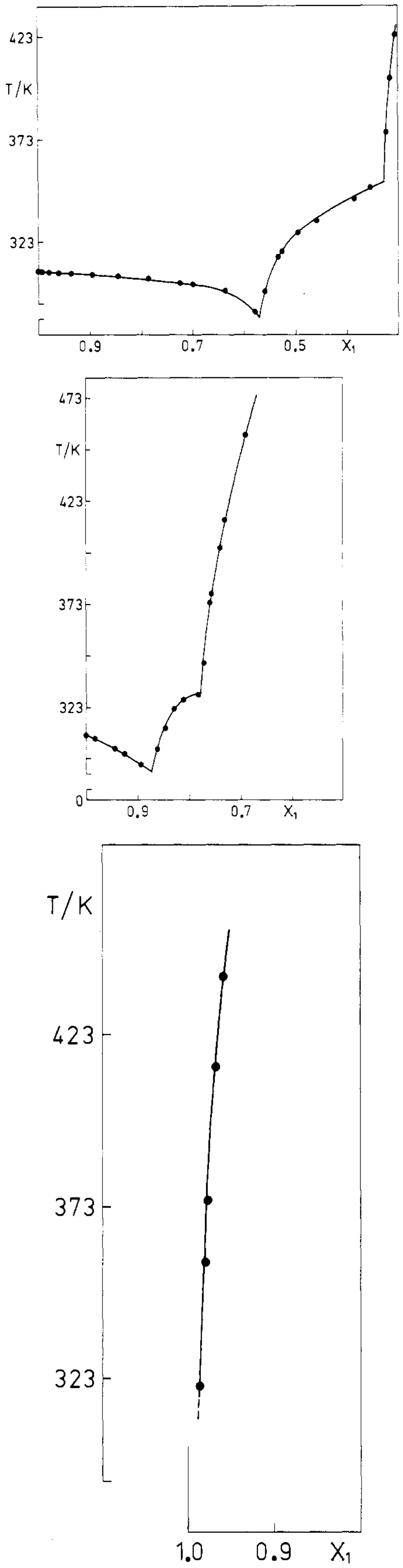

**Figure 1.** Liquid–solid equilibrium temperature in the binary system: (a, upper) 1,3-dioxolan-2-one + $CF_3COONa$; (b, middle) 1,3-dioxolan-2-one + $NaClO_4$; (c, lower) 1,3-dioxolan-2-one + $KClO_4$.

**Table I. Liquid–Solid Equilibrium Temperatures in Binary Systems**

| $X_1$ | $T$/K | $X_1$ | $T$/K |
|---|---|---|---|
| $C_2H_4CO_3$ + $CF_3COONa$ | | $C_2H_4CO_3$ + $NaClO_4$ | |
| | | 1.0000 | 309.35 |
| 1.0000 | 309.35 | 0.9835 | 307.70 |
| 0.9931 | 309.05 | 0.9454 | 302.95 |
| 0.9789 | 308.80 | 0.9270 | 300.30 |
| 0.9604 | 308.60 | 0.8949 | 295.20 |
| 0.9365 | 308.30 | 0.8627 | 303.05 |
| 0.8943 | 307.85 | 0.8481 | 313.20 |
| 0.8457 | 307.05 | 0.8319 | 322.30 |
| 0.7862 | 306.10 | 0.8102 | 326.65 |
| 0.7253 | 303.70 | 0.7839 | 329.00 |
| 0.7005 | 302.95 | 0.7723 | 344.70 |
| 0.6373 | 299.95 | 0.7595 | 374.05 |
| 0.5808 | 294.80 | 0.7564 | 378.90 |
| 0.5594 | 299.70 | 0.7433 | 401.00 |
| 0.5361 | 316.80 | 0.7310 | 414.25 |
| 0.5277 | 318.55 | 0.6870 | 455.70 |
| 0.4951 | 328.30 | | |
| 0.4598 | 334.20 | $C_2H_4CO_3$ + $KClO_4$ | |
| 0.3855 | 344.95 | 1.0000 | 309.35 |
| 0.3561 | 350.30 | 0.9890 | 320.90 |
| 0.3240 | 378.00 | 0.9800 | 356.70 |
| 0.3148 | 403.70 | 0.9770 | 374.65 |
| 0.3078 | 423.75 | 0.9676 | 413.25 |
| | | 0.9596 | 439.60 |

**Table II. Characteristic Points**

| system | $X_{1,E}$[a] | $T_E$/K | $X_{1,P}$ | $T_p$/K |
|---|---|---|---|---|
| $C_2H_4CO_3$–$NaClO_4$ | 0.873 | 291.5 | 0.778 | 330.2 |
| $C_2H_4CO_3$–$CF_3COONa$ | 0.571 | 286.0 | 0.326 | 353.0 |

[a] 1 stands for 1,3-dioxolan-2-one.

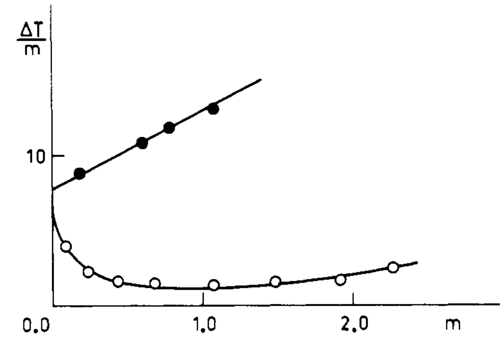

**Figure 2.** Trend of $\Delta T/m$ (where $\Delta T$ is the cryoscopic lowering, $m$ is molality) vs. the molality $m$ of the salt: ●, $NaClO_4$; ○, $CF_3COONa$.

solid equilibrium temperatures that are given in Table I and shown in Figure 1. Figure 1 shows the importance of the ion type on the solubility. Between the two perchlorates, $Na^+$ salt is much more soluble, and between the two $Na^+$ salts, trifluoroacetic acid salt is the more soluble.

These features were also observed in other systems studied previously (*1–3*, *5*). That is, in molten amides the sodium salts are the more soluble and, concerning the anions, those derived from stronger acids promote the solubility of the salts; these salts also promote the building of polymeric structures of amides (*11*, *13*).

In the presently studied mixtures the cation–solvent interaction is not so strong as in electrolytic amide mixtures, where the crystallization does not occur in some concentration ranges.

Two peritectic points are shown. Their coordinates are given in Table II. The nature of these transition points was not investigated, but probably they may be related to incongruently melting intermediate compounds ($NaClO_4 \cdot 3C_3H_4O_3$; $4CF_3COONa \cdot C_3H_4O_3$).

Curves of $\Delta T/m$ vs. $m$ are shown in Figure 2 for $NaClO_4$ and $CF_3COONa$ as solutes, and this figure shows that the behavior of these salts is completely different. The $\Delta T/m$ vs. $m$ curve for $CF_3COONa$ exhibits a trend with a minimum. On the contrary, the curve for $NaClO_4$ is continuously increasing. That is, the deviations from an ideal crystallization curve (*15*) are negative in $NaClO_4$ systems and positive (at low concentrations) in $CF_3COONa$ systems. Probably the first observation may be related to the $Na^+ \leftrightarrow C_3H_4O_3$ interaction, and the second one to the $CF_3 \leftrightarrow CF_3$ interaction.

The value of $\Delta T/m$ extrapolated to $m = 0$ is 7.8 K $mol^{-1}$ kg ($NaClO_4$ solute) and 6.0 K $mol^{-1}$ kg ($CF_3COONa$ solute). The second value is less reliable owing to the shape of the curve. The melting point given in this note does not agree with the value reported in the literature (*16*); this difference may be a consequence of different purity of the sample employed. From the values $T/K = 309.4$ and $K_{cr} = 7.8$ K $mol^{-1}$ kg, $\Delta H = 9.0$ kJ/mol is obtained. Important supercooling phenomena were not observed: only without agitation the mixture with $CF_3COONa$ supercools as much as 10 K in the concentration range, $X(CF_3COONa) \cong 0.45$.

**Registry No.** $CF_3COONa$, 2923-18-4; $NaClO_4$, 7601-89-0; $KClO_4$, 7778-74-7; 1,3-dioxolan-2-one, 96-49-1.

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# Shear Viscosities of Binary Mixtures of Acrylonitrile + Cyclohexane, Benzene, *p*-Xylene, and Mesitylene at 307.4 K

**R. R. Yadava* and S. S. Yadava†**

*Chemistry Department, Gorakhpur University, Gorakhpur 273 009, India*

**Viscosities of binary mixtures of acrylonitrile and nonpolar solvents (viz., cyclohexane, benzene, *p*-xylene, and mesitylene) have been measured at 307.4 K. The mixture viscosities show a marked negative deviation when the mixture is prepared with cyclohexane. However, this deviation has been found to gradually reduce in the case of benzene, *p*-xylene, and mesitylene. The parameter *d* has been calculated from the viscosity data and has been found to be a minimum (most negative value) in the case of cyclohexane. It increases gradually for benzene, *p*-xylene, and mesitylene. The values of interchange energy ($W_{visc}$) have also been calculated and have been found to show the opposite trend to that shown by the parameter *d*, i.e., most positive with cyclohexane, less positive with benzene, and negative and more negative with *p*-xylene and mesitylene, respectively.**

## Introduction

Various attempts have been made to correlate the extent of deviation of viscosity from its rectilinear dependence on the mole fractions and the values of the parameter *d* with the type and the degree of molecular interactions (*1-4*). The molecular interactions between acrylonitrile and some nonpolar aromatics have been already studied in our earlier papers (*5, 6*) by estimation of the dipole moments and it has been suggested that the complex formation is governed by dipole-induced dipole electrostatic attractions.

In order to confirm the earlier conclusion and to establish the suitability of the viscosity measurements for the study of such systems, it has been felt necessary to employ viscosity measurements for the system already studied by dielectric constant measurements.

## Experimental Section

The binary systems studied were acrylonitrile + cyclohexane, acrylonitrile + benzene, acrylonitrile + *p*-xylene, and acrylonitrile + mesitylene. Acrylonitrile (B.D.H., L.R.), cyclohexane (B.D.H., L.R.), benzene (spectroscopic grade), and *p*-xylene and mesitylene (E. Merck) were used. All the chemicals, except that of spectroscopic grade, were purified before use and their purity was checked by density measurements.

The dynamic viscosities ($\eta$), of the liquids and liquid mixtures were measured at 307.4 ± 0.01 K as described elsewhere (*7*). The values of the viscosity were accurate within 0.01%. The densities of the liquids and liquid mixtures were measured pycnometrically. Precautions were taken to avoid losses due to evaporation. The density values were correct to ±0.000 1 g $mL^{-1}$.

Values of the parameter *d* for each sample of all the mixtures were calculated by eq 1, first suggested by Grunberg and

$$\ln \eta_{12} = x_1 \ln \eta_1 + x_2 \ln \eta_2 + x_1 x_2 d \qquad (1)$$

Nissan (*8*), where $\eta_1, \eta_2$ and $x_1$, $x_2$ are the viscosities and mole fractions respectively of the components 1 and 2. $\eta_{12}$ is the viscosity of the liquid mixture. The parameter *d* is proportional

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† Present address: Chemistry Department, Garhwal University Campus, Pauri (Garhwal), India.

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