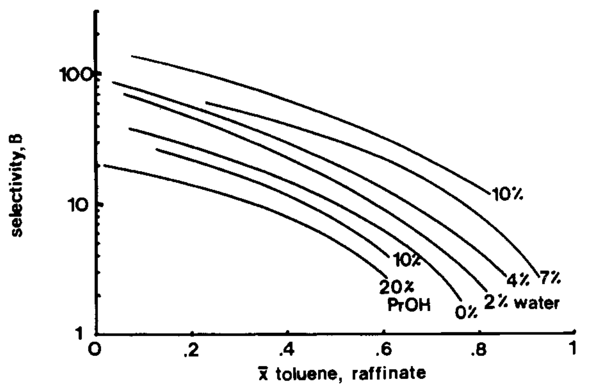

Figure 5. Effect of solvent modifiers on selectivity.

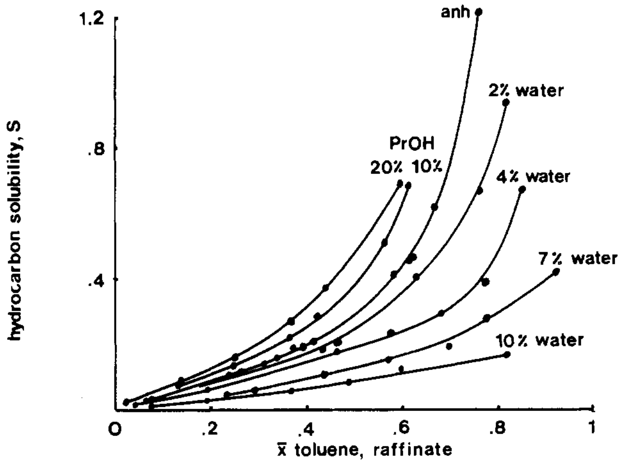

Figure 6. Effect of solvent modifiers on hydrocarbon solubility in the extract phase.

the raffinate, $\bar{x}$. The data have been smoothed in this plot by least-squares fitting to a quadratic line. Figure 6 shows the total hydrocarbon solubility, S, in the extract solvent, $[x(n\text{-heptane}) + x(\text{toluene})]/x(\text{solvent})$, plotted against the solvent-free mass fraction of toluene in the raffinate, $\bar{x}$. It is apparent that increasing the water content in the modified solvent increases the selectivity and reduces the hydrocarbon solubility, while increasing the 2-propanol content reduces selectivity and increases the hydrocarbon solubility. On a mass basis water is a considerably more effective antisolvent than 2-propanol is a prosolvent.

In multistage, countercurrent extraction, using sulfolane, of toluene from a heptane-toluene mixture the extract purity can evidently be increased to any desired level by using a water-modified solvent. This is achieved at the expense of some increase in the solvent throughput owing to the reduced hydrocarbon solubility in the extract solvent. A comparison of the effect of the solvent modifiers on the selectivities with the effect of temperature changes in the *n*-heptane-toluene-sulfolane system may be made by examination of Figures 4 and 5. Here it can clearly be seen that the addition of small amounts (approximately 2% by mass) of water to sulfolane has a more pronounced effect on the solvent selectivity than a decrease in temperature of 25 K.

Glossary

x	liquid-phase mass fraction
β	solvent selectivity = $[x(\text{toluene,extract})/x(\text{toluene, raffinate})]/[x(n\text{-heptane,extract})/x(n\text{-heptane, raffinate})]$
S	hydrocarbon solubility in extract = $[x(n\text{-heptane, extract}) + x(\text{toluene,extract})]/x(\text{solvent,extract})$
$\bar{x}$	solvent-free mass fraction

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Received for review June 22, 1981. Accepted November 23, 1981.

Viscosity of KNO_3–$NaNO_2$–$NaNO_3$ Mixtures

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The viscosities of two molten mixtures of KNO_3–$NaNO_2$–$NaNO_3$ have been measured. Mixture 1 was the eutectic of composition 53/40/7 wt %; the composition of mixture 2 simulated the thermal decomposition of the previous eutectic and was 52/33.6/14.4 wt %. The results can be expressed by $\eta_1(\text{mPa s}) = 0.5631 \exp[-146.9794T^{-1} + (57.4265 \times 10^4)T^{-2}]$ and $\eta_2(\text{mPa s}) = 0.8392 \exp[-498.6183T^{-1} + (68.4889 \times 10^4)T^{-2}]$, respectively.

The eutectic mixture of KNO_3–$NaNO_2$–$NaNO_3$ is known as a heat-transfer medium with many proven advantages. It is safe, nontoxic, noncorrosive, and low-cost, operates at atmospheric pressure, and has exceptional heat-transfer characteristics, thermal stability, and a wide liquid temperature range. In connection with a thermal heat-storage program, the present work was initiated to obtain viscosity data for this molten eutectic and also for a quite similar mixture.

The eutectic KNO_3–$NaNO_2$–$NaNO_3$ mixture (53/40/7 wt % was supplied by Electricité de France, Direction des Etudes et Recherches. The second mixture had the composition 52/33.6/14.4 wt % and was synthetized from Prolabo R.P. Normapur chemicals; this composition was chosen to simulate that of the thermal decomposition of the previous eutectic. In the following, these mixtures will be quoted as mixture 1 and mixture 2, respectively. All salts and mixtures were dried under vacuum for several days at 120 °C.

0021-9568/82/1727-0151$01.25/0

Table I. Viscosity of Mixture 1 (KNO_3-$NaNO_2$-$NaNO_3$ (53/40/7 wt %))

temp, °C	viscosity, mPa s	temp, °C	viscosity, mPa s
482	1.215	184	6.227
482	1.212	184	6.220
482	1.199	184	6.169
318	2.215		
318	2.209	512	1.229
318	2.227	512	1.214
208	4.774	512	1.211
208	4.753		
208	4.739	516	1.236
255	3.290	516	1.264
255	3.236	516	1.194
255	3.257	400	1.593
425	1.414	400	1.610
425	1.416	400	1.571
425	1.394	302	2.545
		302	2.576
186	6.621	302	2.583
186	6.432	240	3.897
186	6.470	240	3.912
373	1.898	240	3.923
373	1.846	519	1.123
373	1.859	519	1.166

Table II. Viscosity of Mixture 2 (KNO_3-$NaNO_2$-$NaNO_3$ (52/33.6/14.4 wt %))

temp, °C	viscosity, mPa s	temp, °C	viscosity, mPa s
480	1.441	216	5.184
480	1.448	216	5.372
480	1.437	216	5.269
382	1.913	349	2.184
382	1.941	349	2.161
382	1.892	349	2.195
326	2.518	482	1.456
326	2.533	482	1.460
326	2.463	482	1.463
254	3.861	443	1.602
254	3.871	443	1.565
254	3.876	443	1.589

The high-temperature viscosimeter and its operation have been described in detail elsewhere (*1*). It is an oscillating viscosimeter with a right-circular cylinder enclosing the liquid sample. The viscosity of the melt is obtained from the measurements of the damping effect of the fluid upon the oscillating pendulum and calculated according the Roscoe's mathematical method (*2*). The experimental vessel, made of refractory stainless steel NS 30, was filled and sealed under purified argon. The viscosity experiments were carried out on the range 200-500 °C, and the successive runs were made either at increasing temperature or at decreasing temperature; some experiments were conducted after an intermediate solidification of the mixture.

We used in calculating the viscosities of mixture 1, the densities reported by Kirst et al. (*3*)

$$\rho = 2.082 \times 10^3 - 0.7288t$$

where ρ is in kg/m^3 and t is in °C. The same expression was used in calculating the viscosity of mixture 2. This hypothesis was found relevant since a calculation based on the additivity of molar volumes yielded a density value differing only by a few thousandths.

Tables I and II report the viscosity results (in mPa s) obtained for mixtures 1 and 2, respectively. For each mixture, the experimental data were fitted to an exponential function of the second order in temperature T (K)

$$\eta = A \exp(BT^{-1} + CT^{-2}) \qquad (1)$$

As underlined by Øye et al.(4-6) this kind of temperature dependence of the viscosity is to be preferred for mixtures to the Arrhenius rule typical for simple liquids. With η in mPa s and T in K, the following numerical values were obtained:

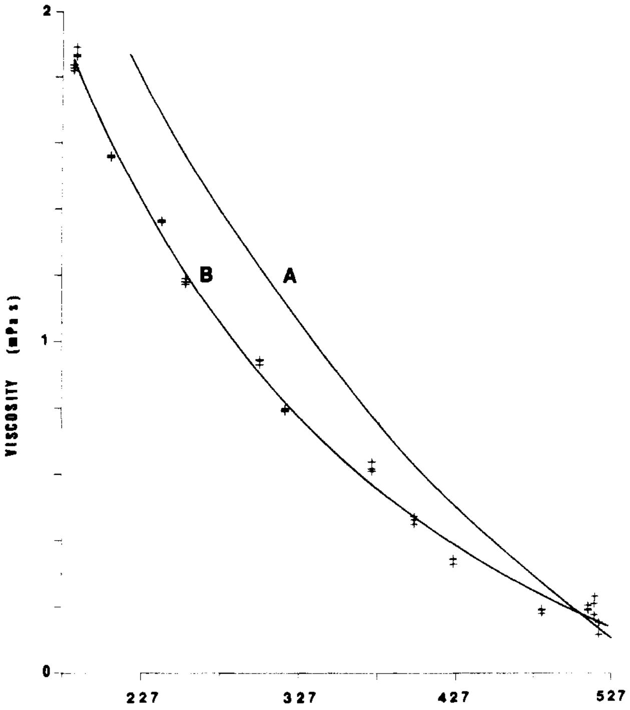

Figure 1. Viscosities of mixture 1 (in mPa s vs. K): (curve A) according to Kirst et al. (*3*), eq 2; (curve B and +) eq 1 and present results.

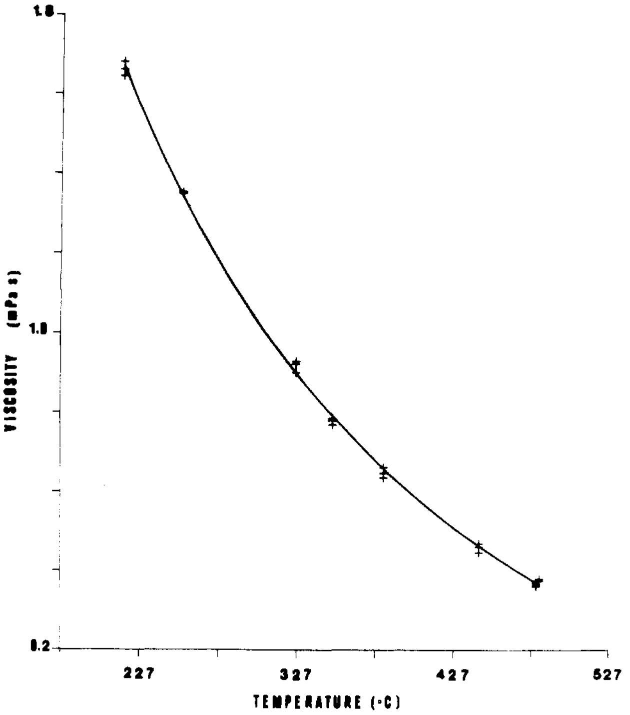

Figure 2. Viscosities of mixture 2 (in mPa s vs. K) from eq 1 and present results.

mixture	A	B	C
1	0.5631	−146.9794	574265.2
2	0.8392	−498.6183	684888.9

Experimental and calculated viscosity values are displayed in Figures 1 and 2, respectively. Figure 1 includes also the viscosities which were measured previously by Kirst et al. (*3*) using a Ostwald viscosimeter; they gave their results as

$$\eta = 67.57 \times 10^{-3} \exp(2247.11/T) \qquad (2)$$

with η in mPa s and T in K, which yields viscosities higher than ours particularly at low temperature.

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Received for review June 29, 1981. Revised manuscript received October 28, 1981. Accepted November 24, 1981. The financial support of Electricité de France, Direction des Etudes et Recherches (Chatou), is gratefully acknowledged.

Solubilities of Some Electrolytes in Water–Pyridine and Water–Acetonitrile Solvent Mixtures

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The solubilities of various organic and inorganic salts have been measured in aqueous pyridine and acetonitrile solutions. For low saturated concentrations of the solute (C_{sat} < 0.1 M), the solubilities are linearly correlated; they are also correlated with the solubilities of nonionic species (e.g., ferrocene).

Introduction

The solubilities of ionic species in various nonaqueous solvents or in solvent mixtures have received renewed interest over the last few years (e.g., ref *1–4*) in order to examine whether they correlate with some solvent parameters such as Kosower's Z index. These data were also used to estimate the medium effect for an electrolyte, which is measured by the free energy change upon transferring 1 mol of the electrolyte (i) from its standard state in water (W) (or in the reference medium) to its standard state in the nonaqueous solvent (S) (or in the solvent mixture):

$$\Delta G°(\mathrm{i}) = n_{\mathrm{i}}[{}^{\mathrm{S}}\mu°(\mathrm{i}) - {}^{\mathrm{W}}\mu°(\mathrm{i})] = n_{\mathrm{i}}RT \ln \gamma_t(\mathrm{i}) \qquad (1)$$

For a 1:1 electrolyte, the transfer activity coefficient $\gamma_t(\mathrm{i})$ is given by the square of the ratio of the mean activity $a_{\pm}(\mathrm{i})$ in water and in S:

$$\gamma_t(\mathrm{i}) = \gamma_{t\pm}(\mathrm{i})^2 = [{}^{\mathrm{W}}a_{\pm}(\mathrm{i})/{}^{\mathrm{S}}a_{\pm}(\mathrm{i})]^2 = {}^{\mathrm{W}}a(\mathrm{i})/{}^{\mathrm{S}}a(\mathrm{i}) \qquad (2)$$

For very dilute solutions, the concentrations can be considered instead of the activities and $\gamma_t(\mathrm{i})$ is given by the ratio of the concentrations of i in water and in S: ${}^{\mathrm{W}}C_{\mathrm{sat}}(\mathrm{i})/{}^{\mathrm{S}}C_{\mathrm{sat}}(\mathrm{i})$.

The literature reports numerous data for solubilities in pure solvents, but few results relevant to solvent mixtures are available. The water-pyridine mixtures (W-Py) have been carefully investigated through their acid-base properties (*5–7*), but only a few solubility data are published (*8–10*). We selected some particular salts such as the picrates, which have been considered in other solvents (*4*, *11–13*), and potassium hexacyanoferrate(III), which has been examined electrochemically in a previous paper (*5*).

In order to develop an electrochemical study of the water–acetonitrile mixtures (W-AN) which is presently in progress, we measured also solubilities in these media, and we selected the same solutes with the view of completing the literature data (*14–17*). (Unfortunately phase separation of the $K_3Fe(CN)_6$ solution occurs in most of the W-AN mixtures and a limited number of results could be obtained. Consequently, we chose to examine another complex of the same charge: the hexamminecobalt(III) chloride.

Table I. Solubilities (−log C_{sat}(i) in the Molar Scale) in Water-Pyridine Mixtures at t = 20 °C

Py, vol %	NEt_4Pic (20 °C)	PyHPic (20 °C)	K_3-$Fe(CN)_6$ (20 °C)	NaCl (25 °C)[a]	KCl (10 °C)[b]	ferrocene (20 °C)
0	1.60	1.97	0.02	−0.79	−0.50	4.47
10	1.07	1.56	0.05		−0.42	3.54
20	0.66	1.19	0.13		−0.34	3.09
30	0.46	0.91	0.30		−0.25	2.65
40	0.31	0.78	0.45		−0.13	2.23
50	0.26	0.67	0.70		−0.07	2.00
60	0.21	0.58	1.15		−0.35	1.68
70	0.21	0.51	1.93	0.22	−0.78	1.37
80	0.18	0.43	3.42	0.75	−1.49	0.97
90		0.38		1.71	−2.27	0.45
100		0.37				0.08

[a] Interpolated from ref *9*. [b] Reference *10*.

Table II. Solubilities (−log C_{sat}(i) in the Molar Scale) in Water-Acetonitrile Mixtures at t = 25 °C

AN, vol %	KPic	NEt_4Pic	PyHPic	Co-$(NH_3)_6$-Cl_3	ferrocene	BPh_4^-[a]
0	1.61		1.97	0.78		3.53
10	1.15	1.04	1.47	0.78	3.58	
20	1.01	0.94	1.21	0.76	3.28	3.34
30	0.85	0.58	0.95	0.81	2.82	
40	0.59	0.35	0.78	0.98	2.57	3.26
50	0.47	0.14	0.62	1.17	2.16	
60	0.59	0.06	0.50	1.43	1.80	3.19
70		0.05	0.43	1.85	1.52	
80		0.01	0.44	2.16	1.32	3.13
90			0.45		1.05	
100					0.73	

[a] Determined from ref *16*.

In addition we determined the solubilities of a particular uncharged species, ferrocene, in order to compare the two series of mixtures.

Experimental Section

Water, AN, Py and Me_2SO were distilled before use. The hexamminecobalt(III) chloride was synthesized (*18*) and analyzed satisfactorily.

The solubility determinations were performed as in other studies (*19*). Saturated solutions of a given solute were prepared by stirring the suspension for 24–48 h in each mixture in a thermostated bath and filtering. The solutions were then

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