Phase Equilibria and Transport Properties in the Systems $AgNO_3/RCN/H_2O$.
$R = CH_3$, C_2H_5, C_3H_7, C_4H_9, C_6H_5, and $C_6H_5CH_2$

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Silver nitrate can form homogeneous liquid phases with some organic nitriles and water, even when there is no miscibility between the pure liquid components. We determined the shapes of the single phase regions in the ternary phase diagram for the following systems: silver nitrate/RCN/H_2O with $R = CH_3$, C_3H_7, C_6H_5, and $C_6H_5CH_2$ at room temperature and for $R = C_6H_5$ also at 60 °C and 0 °C. Furthermore we studied kinematic viscosities, electrical conductivities, and densities of mixtures containing silver nitrate, RCN, and water with the mole ratios $X/4/1$ $(0.2 \leqq X \leqq 3.4)$. In these cases also $R = C_2H_5$ and C_4H_9 were studied. The organic nitriles show different dependences of viscosity and conductivity on the silver nitrate content from the aliphatic ones.

1. Introduction

Organic nitriles, with the exception of acetonitrile, are not miscible with water. Upon the addition of silver nitrate homogeneous solutions can be formed. This phenomenon is based on heteroselective solvation: silver ions and nitrate ions are preferentially solvated by different constituents of the mixed solvents. Strehlow and coworkers [1, 2] were the first to describe this effect quantitatively. They measured the Hittorf transference numbers of acetonitrile and water in silver nitrate/acetonitrile/water (X:4:1) mixtures at small silver nitrate contents X and came to the conclusion that the silver ion solvate complex contains about nine acetonitrile molecules and half a water molecule. The nitrate ion is surrounded by three acetonitrile molecules and three water molecules. Singh, MacLeod, and Parker [3] measured the Walden product of diluted silver nitrate solutions in acetonitrile/water mixtures $(0 \leqq x_{\text{acetonitrile}} \leqq 100\ \text{mol}\%)$. The Walden product drops very sharply up to 20 mol% of acetonitrile. This observation leads to the assumption that the solvodynamic (= Stokes-) radius of the silver ion in acetonitrile/water mixtures increases with increasing acetonitrile concentration.

In order to increase our knowledge about highly concentrated ionic solutions, we first investigated the phase diagrams of some ternary systems silver nitrate/organic nitrile/water. Furthermore, we measured the kinematic viscosity, electrical conductivity and density of some mixtures as functions of the silver nitrate content. In these measurements, solutions with X moles of silver nitrate per 4 moles of organic nitrile and 1 mole of water were used. X was varied between 0.2 and 3.4. In order to study the effect of the size and the shape of the nitriles on the transport properties, a variety of nitriles was used. Acetonitrile CH_3CN (acn), propionitrile CH_3CH_2CN (ppn), butyronitrile $CH_3(CH_2)_2CN$ (bun), and valeronitrile $CH_3(CH_2)_3CN$ (van) represented linear aliphatic species. As aromatic nitriles we used benzonitrile C_6H_5CN (bzn) and phenylacetonitrile $C_6H_5CH_2CN$ (pan).

2. Experimental

2.1 *Preparation of the Solution and Determination of the Ternary Phase Diagrams*

The solutions were prepared in weighing bottles of Duran glass with ground caps. About 20 g of silver nitrate is weighed in the bottle and the desired quantity of water is added. Then the bottle is closed and the mixture is stirred until silver nitrate is dissolved. Now the bottle is weighed again in order to detect possible losses of water. Finally, the desired amount of nitrile is added and the mixture is stirred for 10 min and than

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weighed again. The photosensitive mixtures are stored in a black desiccator under nitrogen atmosphere.

The equilibrium curves in the ternary phase diagrams (tpd) are determined as follows: We used the same weighing bottles as described above. Portions of nitrile and water were added and their respective masses determined, until a desired mole ratio was established. The two phase mixture then was kept at 26 °C under continuous stirring. Now silver nitrate is added in small portions. After stirring the system for 2 minutes it is inspected visually. When the phase boundary has disappeared, the bottle is dried and weighed. Then more silver nitrate is added until a precipitate appears. The total amount of added silver nitrate is now determined by weighing. From the initial masses of nitrile and water and from the masses of silver nitrate at the limits of the one phase region, the mole fractions of the equilibrium phases can be determined. The same procedure was followed to determine the tpd for $AgNO_3/C_6H_5CN/H_2O$ at 60 °C and at 0 °C.

2.2 *Electrical Conductivity Measurements*

For the measurement of the electrical conductivity, we used a conventional cell, made of Duran glass with platinum electrodes. The cell constant was determined with 1 m KCl solution. An audio frequency oscillator (Philips function generator PM 5131) is used as a voltage source. The potential drop at the conductivity cell and the potential drop at a precision resistance of 508.2 Ω in series with the cell were measured using a Philips voltmeter, model PM 2524. The potential difference at the circuit was held constant at 5.0 V by a 1:1 booster. The resistance of the conductivity cell then was calculated by Ohm's law.

The cell resistance was frequency independent in the range 1 kHz ÷ 15 kHz. All conductivity measurements were made at 5 kHz. The temperature in the conductivity cell was maintained at a constant value with a Braun Thermomix 1460 thermostat.

2.3 *Viscosity measurements*

The measurements of the viscosity were performed in Mikro-KPG-Ubbelohde-viscosimeters (Schott-Geräte GmbH. App.-Nr. 68225 $K = 0.03057$ and App.-Nr. 90663 $K = 0.009693$). The efflux times were measured automatically with the electronic clock AVS 300 (Schott-Geräte GmbH). They appear as 6-digit print outs. The temperature of the viscosimeter was maintained at a constant value with a Braun Thermomix 1460.

3. Results

3.1 *Ternary Phase Diagrams*

Figure 1 shows Gibbs phase triangles for three systems. Only acetonitrile is completely miscible with water. The saturation curve in this system is in accordance with values reported earlier by Moolel and Schneider [4]. For the other systems, RCN and H_2O are not miscible. By addition of silver nitrate, homogeneous three component regions appear. As seen in Fig. 2, in the case of benzonitrile the one phase region at 26 °C is very narrow at higher water concentrations. At 0 °C two separated one phase fields occur. At 60 °C a larger one phase region is observed.

It is interesting to see that the maximum solubility of silver nitrate in RCN/H_2O mixtures seems to be quite independent of R and always occurs at a nitrile to water ratio close to 4:1.

3.2 *Transport Properties*

In order to be able to cover a wide range of silver nitrate concentrations, the experiments were done in RCN/H_2O mixtures with a mole ratio 4:1. The kinematic viscosity, electrical conductivity and density were measured in the temperature range from 20 to 60 °C. From these data the molar conductivities and the viscosities can be calculated. By interpolation, values for 30 °C are determined. These data are collected in Table 1. Furthermore, they are displayed in Figs. 3, 4, and 5. Arrhenius plots of the electrical conductivity and of the viscosity always lead to straight lines. The activation energies, obtained from these plots, are shown in Figs. 6 and 7.

4. Discussion

The system silver nitrate/acetonitrile/water has already been studied by Schneider and Strehlow [1]. Our findings, as displayed in Fig. 1, are in good accord with their results. While acetonitrile and water are completely miscible at room temperature, butyro-

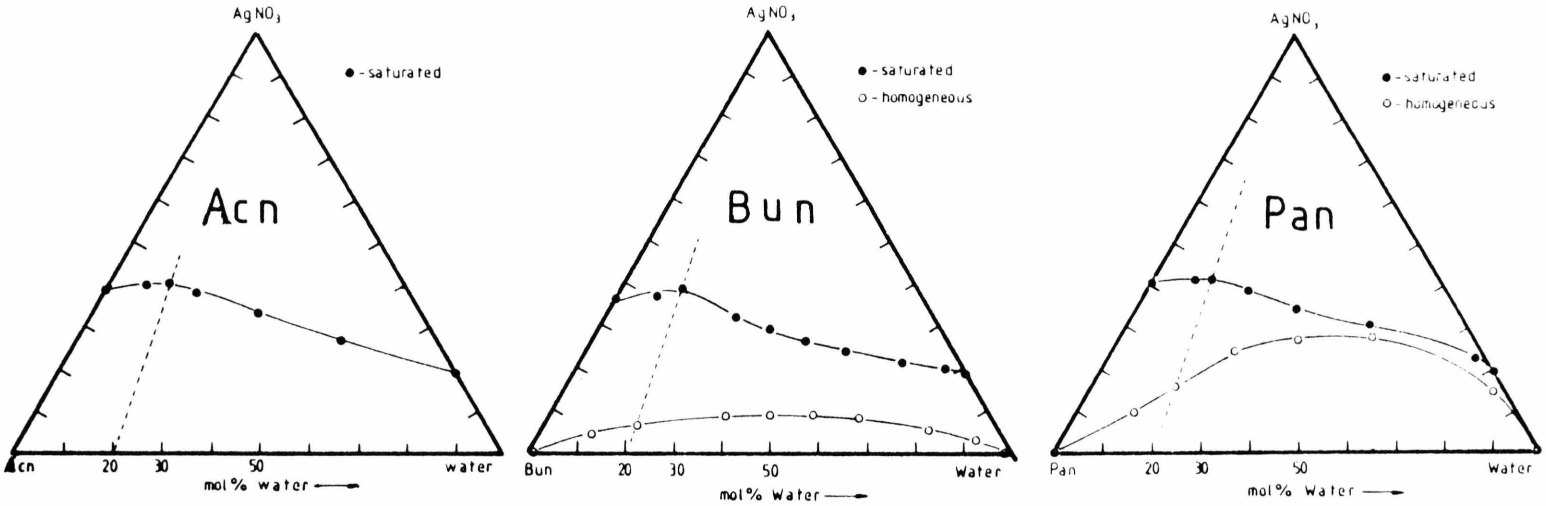

Fig. 1. Representation of the one phase region in the Gibbs phase triangle for the systems defined in the figure. $T = 26\,^\circ C$.

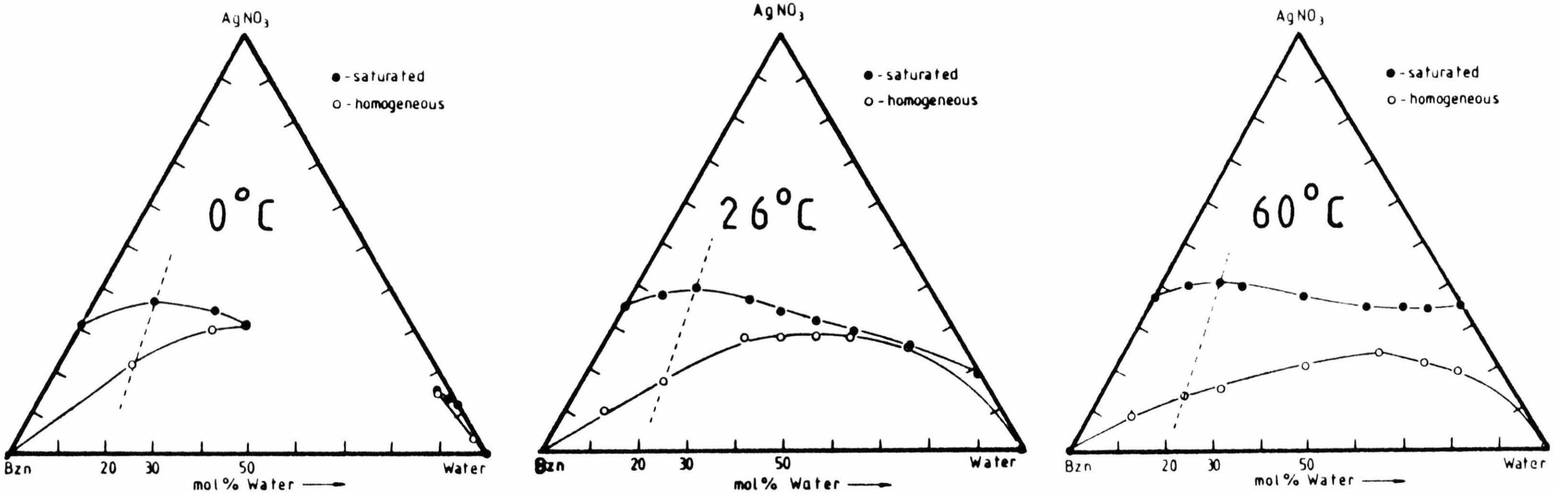

Fig. 2. Representation of the one phase region in the Gibbs phase triangle for silver nitrate/benzonitrile/water at 0 °C, 26 °C, and at 60 °C.

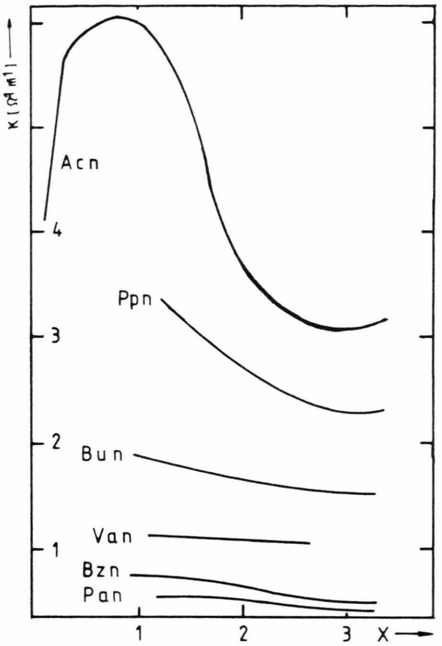

Fig. 3. Electrical conductivities of $AgNO_3/RCN/H_2O$ mixtures at 30 °C versus the silver nitrate content X. Total composition X:4:1. R is defined in the figure.

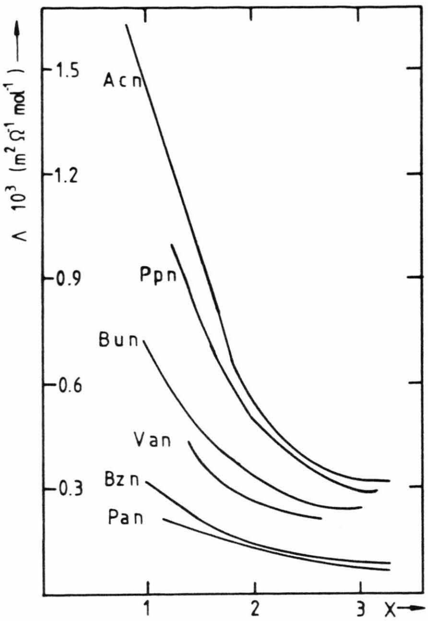

Fig. 4. Formal molar conductivities of $AgNO_3/RCN/H_2O$ mixtures. X: see legend to Figure 3.

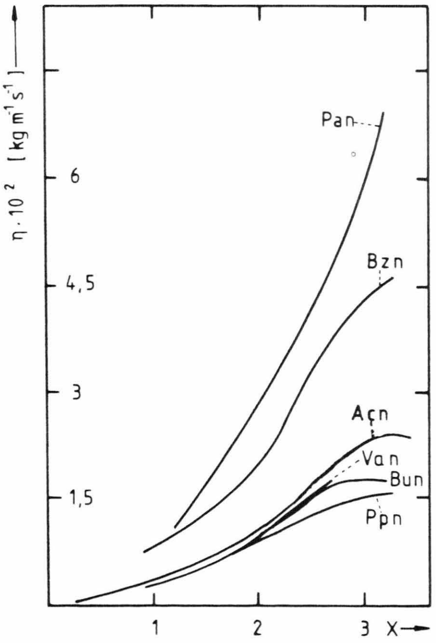

Fig. 5. Viscosity of $AgNO_3/RCN/H_2O$ mixtures. X: see legend to Figure 3.

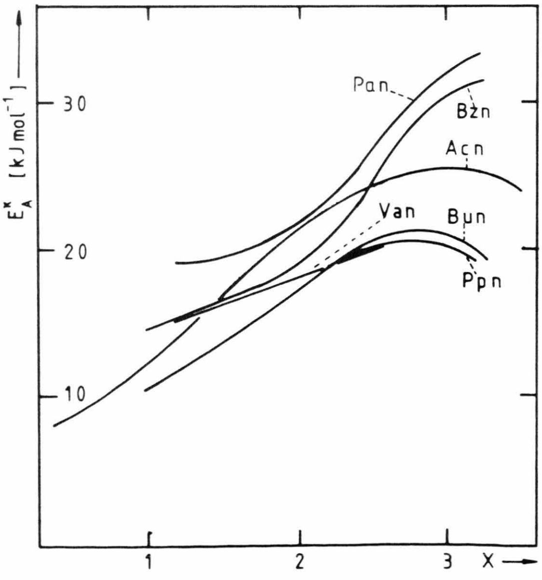

Fig. 6. Activation energies of the electrical conductivity for mixtures $AgNO_3/RCN/H_2O$. X: see legend to Figure 3.

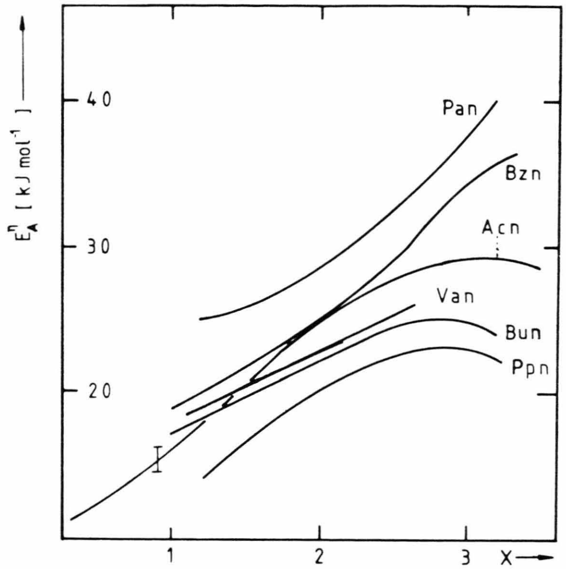

Fig. 7. Activation energies of the viscosities of $AgNO_3$/RCN/H_2O mixtures. X: see legend to Figure 3.

Table 1. Densities, conductivities, molar conductivities, and viscosities of silver nitrate/nitrile/water mixtures at 30 °C. Mole ratios X:4:1.

X	d [kg m^{-3}]	k [Ohm^{-1} · m^{-1}]	$\lambda \cdot 10^4$ [m^2 Ohm^{-1} · mol^{-1}]	$\eta \cdot 10^3$ [kg m^{-1} · s^{-1}]
1. acetonitrile				
0.18	995	4.16	52.60	0.72
0.40	1048	5.68	36.70	0.81
0.90	1348	5.97	15.40	2.30
1.20	1479	5.70	12.96	3.28
1.80	1738	4.31	6.70	8.02
2.30	1912	3.50	4.62	13.93
2.80	2160	3.36	3.79	20.34
2.87	2143	3.16	3.36	21.62
2.95	2174	2.96	3.11	22.69
3.09	2214	2.90	2.96	25.70
3.22	2241	3.00	3.15	24.10
3.30	2242	3.09	3.14	24.30
3.42	2246	3.12	3.16	24.20
2. propionitrile				
1.20	1344	3.35	9.18	3.08
2.30	1712	2.67	4.25	10.65
3.10	1881	2.24	3.18	16.14
3.24	1888	2.28	3.06	15.94
3. butyronitrile				
1.00	1187	1.84	7.18	2.96
1.80	1430	1.68	3.91	8.05
2.32	1581	1.50	2.81	12.60
2.70	1674	1.46	2.42	16.97
3.02	1694	1.42	2.23	17.01
3.26	1699	1.45	2.26	17.08
4. valeronitrile				
1.20	1180	1.12	4.35	3.98
1.75	1347	1.12	3.02	7.92
2.22	1456	1.07	2.41	11.65
2.60	1466	1.04	2.14	16.19
5. benzonitrile				
0.95	1303	0.67	3.20	7.57
1.20	1369	0.75	2.88	6.90
2.30	1653	0.57	1.24	26.61
3.00	1736	0.50	0.86	43.76
3.25	1736	0.49	0.86	46.03
6. phenylacetonitrile				
1.20	1332	0.52	2.21	10.58
2.30	1581	0.52	1.26	34.06
3.00	1693	0.40	0.79	59.73
3.20	1773	0.37	0.68	98.93

nitrile and water are completely immiscible. They become miscible, when only ten mol% of silver nitrate are added to the mixture. In the case of aromatic nitriles, the miscibility gaps extend much more into the interior of the phase triangle, indicating that higher concentrations of silver nitrate are necessary to form a one phase region. This different behavior of aliphatic and aromatic nitriles cannot be traced back to a different affinity of the nitriles towards silver nitrate: the solubility of silver nitrate in the pure nitriles is nearly the same for all systems investigated in this study.

We wanted to measure the transport properties over a wide range of silver nitrate concentrations without changing the composition of the solvent. The dotted lines in Figs. 1 and 2, corresponding to mole ratios X:4:1, characterize the investigated systems.

Only in the case of acetonitrile, a concentration range, in which the specific conductivity increases with increasing salt concentration can be realized, see Figure 3. At $X = 1$ the specific conductivity shows a maximum, followed by a steep decrease. For the larger nitriles, this decrease at $X \geqq 1$ also can be observed. Only in the case of valeronitrile, the conductivity is nearly independent of X.

The formal molar conductivities decrease with increasing X in all investigated cases (Figure 4). This decrease is accompanied by an increase of the dynamic viscosity, Figure 5.

The decrease of the formal molar conductivity with increasing X can either be caused by strong ion pair formation or by the pronounced increase of the viscosity. In the latter case, the Walden rule should be followed by the systems. This rule can be stated as a relationship between the activation energies for the

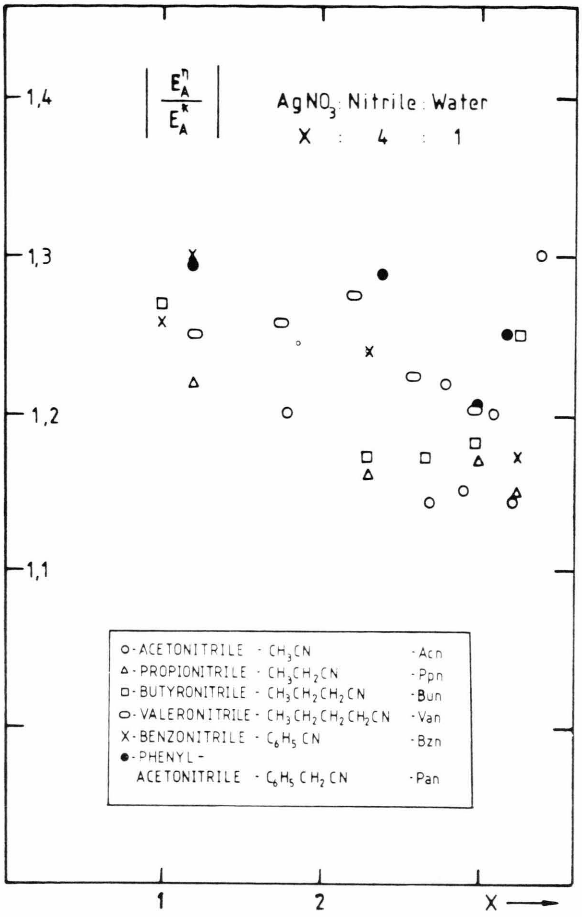

Fig. 8. Ratio of the activation energies of the electrical conductivities and the viscosities of $AgNO_3/RCN/H_2O$ mixtures. Symbols see insert.

conductivity and for the viscosity:

$$E_A^k = -E_A^\eta .$$

In Figs. 6 and 7 we show the activation energies as functions of X. They were determined from Arrhenius plots. While the activation energies in the systems R = aliphatic group vary only little with X and show a maximum around $X = 2.8$, the activation energies for R = aromatic group increase monotonously with X. Nevertheless, there is a correlation between the activation energies of the transport properties: In Fig. 8 the ratios $|E_A^\eta/E_A^k|$ are plotted versus X. This ratio is always > 1, but despite the fact that the activation energies themselves are found in the region between about 10 kJ/mol and 40 kJ/mol, the ratios always lie between 1.15 and 1.3 and do not vary systematically with either X or R.

Bearing in mind that at higher X, the amount of salt is only little smaller than the amount of solvent, formation of ion pairs appears to be very likely. These large ion pairs contribute to the increase of the viscosity as well as to the decrease of the conductivity. We will discuss this matter in more detail in a forthcoming publication, in which measurements of self diffusion coefficients in such systems are reported [5].

Acknowledgements

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