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Transport Properties of Lithium Nitrate and Calcium Nitrate Binary Solutions in Molten Acetamide

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Viscosity and electrical conductivity were measured for eutectic binary mixtures of $LiNO_3$– and $Ca(NO_3)_2$–CH_3CONH_2 in the range of 290–329 K. The complex behavior of these solutions is discussed as aggregation phenomena of solvated ions.

Introduction

Some experimental evidence exists for the complexity of electrolytic solutions in molten acetamide. Cryoscopic measurements (*1–3*) showed that solute–solvent interactions become very important with decreasing temperature (i.e., with increasing electrolyte concentration). Around the eutectic concentration (when the electrolyte is an alkali metal salt of strong acids) the mixture supercools and in some cases (sodium salt) the crystallization does not occur at all even if the mixture is stirred and crystalline nuclei are added. These supercooled liquids exhibit viscoelastic behavior (*4*) and high ultrasonic losses (*5*, *6*) in the megahertz region that can be related to aggregation phenomena of solvated ions. In this note we present the results of measurements of viscosity and electrical conductivity performed on $LiNO_3$– and $Ca(NO_3)_2$–CH_3CONH_2 binary mixtures.

Experimental Section

Conductivity. The electrical conductivity was measured with a H. Tinsley and Co. Ltd. electrolytic bridge and a Phylips conductivity cell, checked by means of potassium chloride solutions. The cell constant was calculated by using the mean values of specific conductivity of KCl solutions given by Kohlrausch and Jones (*7*).

Viscosity. The viscosity coefficient was measured by means of a Hoeppler viscosimeter previously described (*8*), using the ball which gives a falling time in the range suggested by the manufacturer. The density was measured with a conventional pycnometric method with a Lauda ultrathermostat (±0.05 K). The chemicals employed are Fluka CH_3CONH_2 and Carlo Erba RPE $LiNO_3$ and $Ca(NO_3)_2$. The salts were dried under dynamic vacuum at 180 °C. Acetamide was purified by sublimation and dried under dynamic vacuum at room temperature.

Table I. Viscosity Values (η) as a Function of T

T, K	η, cP	T, K	η, cP
$LiNO_3$ (1)–CH_3CONH_2 (2), x_2 = 0.7960			
289.5	656.2	297.7	303.7
291.9	498.2	300.6	279.8
293.8	385.4	304.1	184.1
$Ca(NO_3)_2$ (1)–CH_3CONH_2 (2), x_2 = 0.8760			
314.3	191.8	323.3	101.2
317.3	145.8	326.8	84.0
320.8	117.8		

Table II. Specific Electrical Conductivity (χ) as a Function of T

T, K	$10^4\chi$, Ω^{-1} cm^{-1}	T, K	$10^4\chi$, Ω^{-1} cm^{-1}
$LiNO_3$ (1)–CH_3CONH_2 (2), x_2 = 0.7960			
289.6	4.45	296.3	7.36
291.7	5.25	299.5	9.14
294.0	6.25	302.4	11.08
$Ca(NO_3)_2$ (1)–CH_3CONH_2 (2), x_2 = 0.8760			
313.8	9.42	323.5	15.58
316.5	10.80	326.8	18.00
319.6	12.86		

Results and Discussion

The experimental results of viscosity are given in Table I and shown in Figure 1 as an Arrhenius plot. Specific electrical conductivity is given in Table II. In Figure 2 the trend of equivalent conductivity Λ vs. temperature is shown as an Arrhenius plot.

From these results, the following observations may be made: (1) The Ca^{2+} solutions have larger equivalent conductivities than the corresponding Li^+ solutions. (2) The slope in the plot of ln Λ vs. $1/T$ is higher for Ca^{2+} solutions. (3) Viscosity is higher for Ca^{2+} solutions. (4) The slope in a plot of ln η vs. $1/T$ is higher for Li^+ solutions.

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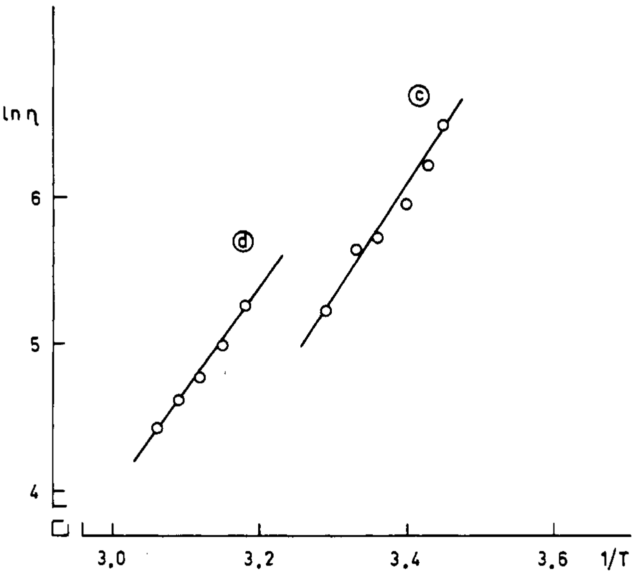

Figure 1. ln η vs. $1/T$: (c) $LiNO_3$ (1)–CH_3CONH_2 (2); (d) $Ca(NO_3)_2$ (1)–CH_3CONH_2 (2).

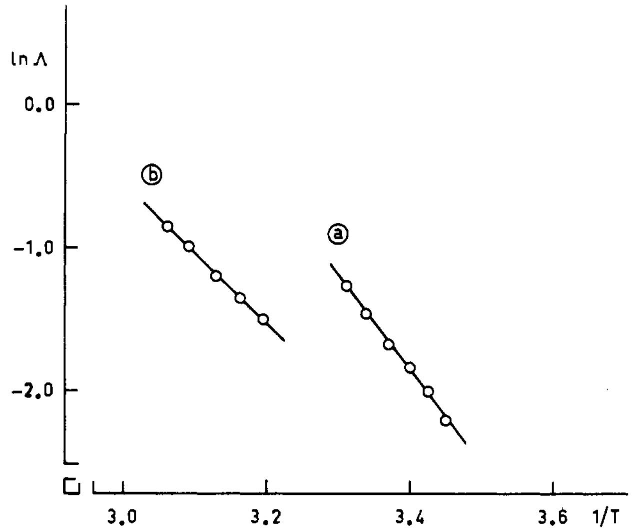

Figure 2. ln Λ vs. $1/T$: (a) $LiNO_3$ (1)–CH_3CONH_2 (2); (b) $Ca(NO_3)_2$ (1)–CH_3CONH_2 (2).

These solutions, as pointed out previously (*3*), present a complex behavior that, following cryoscopic and ultrasonic investigations (*3–6*), may be explained on the basis of aggregation phenomena of solvated ions. The conductivity is higher for Ca^{2+} solutions and this fact is in line with the higher charge of this ion. The viscosity of Ca^{2+} solutions is higher and is probably due to the following mechanism of equilibria:

$$MX \rightleftarrows M^+ + X^-$$

$$M^+ + xS \rightleftarrows MS_x^+$$

$$X^- + yS \rightleftarrows XS_y^-$$

$$MS_x^+ + XS_y^- + nS \rightleftarrows \text{aggregate}$$

The fact that the viscosity of Ca^{2+} solutions is higher than Li^+ solutions means that the aggregates in Ca^{2+} solutions are more extended in comparison with aggregates in Li^+ solutions.

The slope in the Arrhenius plots must be regarded as a temperature coefficient and not as a true E_{act}/R, owing to equilibria involved in these solutions.

The fact that the temperature coefficient of the equivalent conductivity is higher for Ca^{2+} solutions may also be explained in terms of the suggested equilibria; i.e., the temperature increase affects the equilibrium aggregates and the resulting free ions increase the conductivity.

The temperature coefficient of viscosity is higher for Li^+ solutions and this experimental evidence may be explained with the following argument: the aggregates with Li^+ ions are less stable than the aggregates with Ca^{2+} ions, also borne out by our cryoscopic measurements.

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Glossary

η	viscosity, cP
Λ	equivalent conductivity
χ	specific electrical conductivity, Ω^{-1} cm^{-1}

Registry No. $LiNO_3$, 7790-69-4; $Ca(NO_3)_2$, 10124-37-5.

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Vapor–Liquid Equilibria of the System Trimethyl Borate (1)–*n*-Heptane (2)

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Vapor–liquid equilibria for the binary system trimethyl borate (1)–*n*-heptane (2) have been measured at 101 325 Pa. Data have been checked for thermodynamic consistency and also correlated by Wilson equations.

The isobaric vapor–liquid equilibria of the trimethyl borate (1)–*n*-heptane (2) system were measured at 101 325 ± 133 Pa (760 ± 1 torr). An Altsheler still (circulation type) was used and is described in detail by Hala et al. (*1*). The present version incorporates two thermocouples, one near the surface of the

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