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Transport Properties in Molten Alkylammonium Chlorides. II. $C_2H_5NH_3Cl + (C_2H_5)_2NH_2Cl$

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The system $C_2H_5NH_3Cl$ (A) + $(C_2H_5)_2NH_2Cl$ (B) was examined with the aim of determining the phase diagram and the transport properties. The phase diagram is of the simple eutectic type, with eutectic temperature $T_e = 350$ K and eutectic composition $x_B = 0.32$ in mole fraction. Densities, conductivities, and viscosities of the molten mixtures were measured in the whole composition range, for $0 < x_B < 1$. From the collected experimental data, it results that the considered properties of the system do not behave additively as a function of composition. The experimental data of conductivity and viscosity show an Arrhenius behavior.

Introduction

Alkylammonium chlorides, like other salts of substituted ammonium cations, are a particularly interesting class of compounds, owing to the possibility of tailoring the volume and shape of the organic cation by introducing different hydrocarbon chains. Moreover, they have found wide application as reagents in analytical and organic chemistry, as well as in electrochemistry as supporting electrolytes. In previous work by this research group, the thermal properties and thermal stability of some systems of alkylammonium chlorides with linear hydrocarbon chains have been reported (Kisza et al., 1981, 1982; Zabinska et al., 1991). In particular in the first paper of this series the binary system formed with the two shortest homologues of the family of the monosubstituted alkylammonium chlorides was examined, viz., the system CH_3NH_3Cl + $C_2H_5NH_3Cl$ (Zabinska et al., 1991). That system was proved to be of the eutectic type and to display a nonideal behavior. It was also experimentally observed that ethylammonium chloride can be a very suitable component of such molten salt systems, inasmuch as it gives a clear, relatively stable and nonvolatile melt at moderate temperatures, i.e., at $T > 386$ K (Zabinska et al., 1991).

In the present paper a second binary system containing ethylammonium chloride [(EA)Cl], the system $C_2H_5NH_3Cl + (C_2H_5)_2NH_2Cl$, is considered. The liquidus curves of the phase diagram have been determined. Molar volumes, conductivities, and viscosities of molten mixtures have been measured. On the basis of the information collected, one can evaluate the influence of ion size, acid−base characteristics, and intermolecular interactions on the structure of the melt in the binary system.

Experimental Section

Materials. The salts were prepared by neutralization of the amines (both Fluka, ethylamine purum 70% in water, diethylamine purum > 99%) with HCl (Polskie Odczynniki Chemiczne [P. O. Ch.], Gliwice, Poland; czysty [pure]) according to the procedure previously described (Zabinska et al., 1991). Their melting point was checked by means of microscopic observation with a Boetius-type apparatus. The pure components, as well as the binary mixtures prepared by melting the preweighed salts in nitrogen atmosphere, were stored under vacuum before use.

For the phase diagram, ethylamine hydrochloride, 98%, and diethylamine hydrochloride, 99%, both supplied by Aldrich, were used as received, except for the fact that they were kept under vacuum 48 h at 353 K before preparing the mixtures. The mass measurements were done on a single Mettler balance (model H 10) within the precision of ±0.0001 g. The possible error in the mole fraction is less than ±0.001.

Transport Measurements. The temperature range in which transport properties were measured was $400\ \text{K} < T < 530$ K. In particular, in the case of conductivity, the temperatures of the molten mixtures were controlled with the platinum thermomether Pt-100 immersed inside the cell.

The pure components and nine fused mixtures of composition $0.1 < x_B < 0.9$ (component B being diethylammonium chloride [(DEA)Cl]) were examined. For each measurement, the sample mass was 20−60 g. The accuracy of weighing was ±0.0002 g.

The considered properties were determined by means of the previously described techniques (Zabinska et al., 1991; Kisza et al., 1980).

Densities were measured with a pycnometric method with fused ethylammonium chloride as a standard. All the values are an average of at least five readings. The volume of the pycnometer was $V/\text{cm}^3 = 0.287(\pm0.003)h \pm 5.197(\pm0.008)$ with $R = 0.999$. On the basis of this equation, the estimated uncertainty of density was $\pm0.005\ \text{g·cm}^{-3}$.

For conductivity, a cell of termisil glass with a capillary-type electrode was used. The electrode possessed two platinum rings sealed in a glass tube (inside and outside) and separated by a vertical glass capillary. The cell constant was determined by means of a standard solution

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of 1 M KCl in water at 298 K and was found to be (57.39 ± 0.03) cm^{-1}. Conductivities were measured with an automatic RLC bridge type E-318 (Meratronik, Szczecin, Poland) at 1 kHz. The reported values are an average of at least five to six measurements, with a precision of ± 0.1% and an estimated uncertainty of $\pm 1 \times 10^{-4}$ $S \cdot cm^{-1}$.

A modified Ostwald-type viscosimeter was used for viscosity measurements with three Pt electrodes. The flow time of the constant volume of liquid between two electrodes through a glass capillary was measured by an electronic quartz clock; the third electrode provided the electric contact. At least five to six readings differing in value ≤0.5 s from each other were taken into account (in the range of 100 s). The viscosimeter was calibrated using molten ethylammonium chloride as the standard substance; the dependence of viscosity from the time of outflow was linear, according to the equation $\eta/\text{Pa}\cdot\text{s} = 4.07 \times 10^{-5} (\pm 0.06 \times 10^{-5})t - 0.0026(\pm 0.0002)$ with $R = 0.996$. The estimated uncertainty in these measurements was $\pm 0.5 \times 10^{-3}$ Pa·s.

Phase Diagram Determination. Visual polythermal analysis and differential scanning calorimetry (dsc) were adopted as reported in the cited work (Zabinska et al., 1991). After use for visual determination, small samples (2−10 mg) of some mixtures were submitted to dsc with a Perkin-Elmer DSC-2 instrument calibrated as previously described (Zabinska et al., 1987). Owing to the remarkable volatility of component B above 450 K, the results of dsc analysis were not very reproducible in the region of the diagram richer in diethylammonium chloride, and sublimation peaks were always recorded at higher temperatures. These phenomena made it rather difficult to single out by means of dsc the melting enthalpy for pure (DEA)Cl. However, this enthalpy was evaluated taking into account only the first peak occurring approximately at 503 K and neglecting the subsequent thermal effects due to sublimation and/or decomposition that took place immediately after the fusion peak.

The collected results are the average of at least five measurements taken on three to five samples for each composition. The precision in T measurements was ±1 K.

Results and Discussion

Ethylammonium and diethylammonium hydrochlorides used in the present study melted at (384 ± 2) K and (503 ± 2) K, with enthalpy of fusion (5.5 ± 0.4) kJ mol^{-1} and (15 ± 1.5) kJ mol^{-1}, respectively. Besides the solid-to-solid phase transition previously found in (EA)Cl at (355 ± 3) K with $\Delta_{trs}H_m = (11 \pm 1)$ $kJ \cdot mol^{-1}$ (Zabinska et al., 1991), also in (DEA)Cl a phase transition in the solid state, not mentioned in the previous literature, was detected by dsc as a twin peak at (372 ± 2) K with $\Delta_{trs}H_m = (5 \pm 1)$ kJ mol^{-1}.

The experimental transition temperatures measured by dsc and visual polythermal analysis on the mixtures of the considered system are reported in Table 1. The phase diagram obtained is illustrated in Figure 1.

The visual changes associated with the crystallization phenomena in the region of the diagram richer in component A were easily detected inasmuch as pure ethylammonium chloride crystallized starting from the bottom of the Pyrex ampule, whereas the crystals of the eutectic mixture began to appear in the bulk of the molten sample.

From visual observation confirmed by dsc measurements, this system was found to be of the simple eutectic type, with $T_e = (350 \pm 3)$ K and $x_{B,e} = 0.32$ in mole fraction.

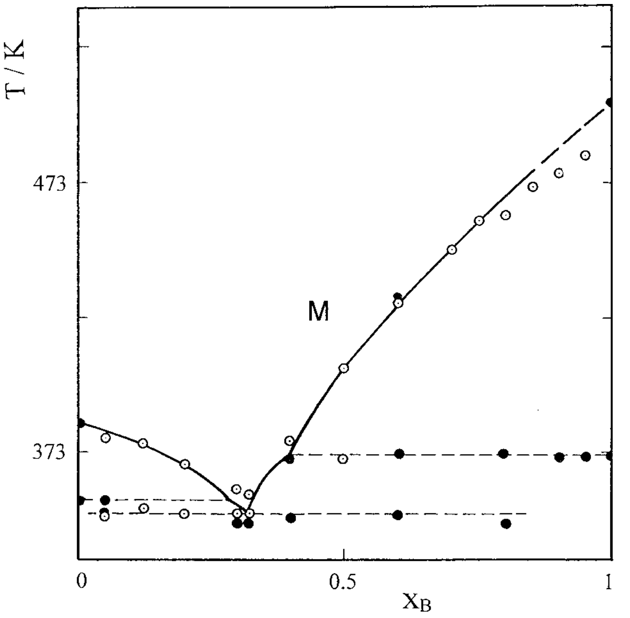

Figure 1. Phase diagram of the system $C_2H_5NH_3Cl$ (A)−$(C_2H_5)_2NH_2Cl$ (B): (○) visual observation; (●) dsc data.

Table 1. Phase Transition Temperatures in Binary Mixtures of $C_2H_5NH_3Cl$ (A) + $(C_2H_5)_2NH_2Cl$ (B) (dsc = Differential Scanning Calorimetry; vis = Visual Polythermal Analysis)

x_B	T/K (dsc)	T/K (vis)	x_B	T/K (dsc)	T/K (vis)
0.00	355		0.60	349	
	384			373	
0.05	355			431	428
	350	349	0.70		448
		378	0.75		459
0.12		352	0.80	346	
		376		373	
0.20		350			461
0.30	346	350	0.85		471
		359	0.90	371	
0.32	346	350			476
0.40	348		0.95	371	
	371	377			483
0.50		371	1.00	372	
		404		503	502

The experimental data for density, electrical conductivity, and viscosity as a function of temperature for the pure salts and their mixtures of the given compositions are summarized in Tables 2−4, where the data for (EA)Cl and (DEA)Cl are those previously reported (Zabinska et al., 1991; Gatner and Kisza, 1969).

The temperatures of transition and fusion of the pure components as determined by dsc in the present work are in good agreement with previous literature data. The melting mechanism of (EA)Cl (component A) was briefly discussed in the mentioned paper (Zabinska et al., 1991). Just above the fusion temperature, this salt gives a fairly stable and clear molten phase, in which no sublimation or decomposition phenomena are apparent in the time scale of the measurements.

On the other hand, the thermal behavior of pure (DEA)Cl (component B) requires a more detailed discussion. Blazejowski and Kowalewska (1986), in a paper devoted to the thermal stability of many amine hydrochlorides, reported several melting points taken from early and recent literature, although they did not monitor the fusion process. Among these data, one can quote, for example, the melting temperature given by Stone and co-workers (1958) at (496

Table 2. Experimental Densities ($\rho_{AB} \pm 5 \times 10^{-3}$)/g·cm^{-3} of Molten $C_2H_5NH_3Cl$ (A) + $(C_2H_5)_2NH_2Cl$ (B) Mixtures at Selected Temperatures

	x_B										
T/K	0.00	0.09	0.20	0.30	0.39	0.49	0.60	0.70	0.77	0.88	1.00
413	0.997	1.004									
423	0.992	0.997									
433	0.988	0.993	0.990	0.995	0.974						
443	0.983	0.988	0.986	0.990	0.967	0.953	0.959				
453	0.979	0.984	0.981	0.985	0.960	0.945	0.951				
463	0.975	0.978	0.977	0.979	0.955	0.939	0.943	0.939			
473	0.970	0.971	0.973	0.975	0.948	0.932	0.938	0.931	0.933		
483	0.966		0.968	0.970	0.942	0.925	0.932	0.924	0.926	0.932	
493	0.962			0.964	0.938	0.920	0.926	0.919	0.920	0.926	
498											0.906
503	0.957					0.913	0.919	0.914	0.915	0.921	0.904
508											0.902
513						0.907	0.911	0.907	0.910	0.914	0.900
518											0.898
523									0.902		0.896

Table 3. Experimental Conductivities ($k_{AB} \pm 1 \times 10^{-4}$)/S·cm^{-1} of Molten $C_2H_5NH_3Cl$ (A) + $(C_2H_5)_2NH_2Cl$ (B) Mixtures at Selected Temperatures

	x_B										
T/K	0.00	0.09	0.20	0.30	0.39	0.49	0.60	0.70	0.77	0.88	1.00
413	0.0858	0.0785	0.0689	0.0606	0.0542	0.0492					
418		0.0831		0.0639	0.0579	0.0519					
423	0.0968	0.0883	0.0783	0.0691	0.0624	0.0554					
428		0.0933	0.0833	0.0726	0.0675	0.0592	0.0555				
433	0.1082	0.0985	0.0886	0.0782	0.0715	0.0630	0.0604				
438		0.1041	0.0929	0.0817	0.0747	0.0670	0.0631				
443	0.1170	0.1090	0.0978	0.0870	0.0793	0.0714	0.0669				
448		0.1141	0.1030	0.0918	0.0838	0.0756	0.0709				
453	0.1304	0.1189	0.1080	0.0972	0.0892	0.0798	0.0747	0.0650			
458		0.1229	0.1143	0.1004	0.0918	0.0841	0.0789	0.0690			
463	0.1403	0.1280	0.1194	0.1055	0.0972	0.0883	0.0825	0.0785	0.0744		
468		0.1344	0.1237	0.1097	0.1007	0.0927	0.0869	0.0821	0.0783		
473	0.1542	0.1399	0.1280	0.1140	0.1027	0.0972	0.0913	0.0867	0.0820		
478			0.1310	0.1181	0.1067	0.1016	0.0958	0.0910	0.0859		
483				0.1222	0.1122	0.1053	0.0995	0.0949	0.0900	0.0849	
488				0.1263	0.1160	0.1090	0.1036	0.0988	0.0934	0.0872	
493				0.1318	0.1214	0.1131	0.1078	0.1027	0.0972	0.0915	
498						0.1179	0.1123	0.1067	0.1003	0.0942	0.0850
503						0.1233	0.1169	0.1105	0.1046	0.0980	0.0882
508						0.1279	0.1212	0.1143	0.1082	0.1015	0.0914
513						0.1326	0.1258	0.1174	0.1129	0.1045	0.0929
518						0.1369	0.1303	0.1205	0.1167	0.1069	0.0977
523						0.1398	0.1342	0.1247	0.1207	0.1100	0.1010

± 5) K. A higher melting point was found by Airoldi (1985) at 501 K.

In the present work, an attempt was made to prepare a small amount of a purer sample of this compound by means of two recrystallizations of the Aldrich reagent from ethanol. The melting peaks of the salt recrystallized twice were better defined, but it also melted at 503 K with an approximate fusion enthalphy of 15 kJ·mol^{-1}. Therefore its thermal behavior was not actually different from that of the starting Aldrich product. Because sublimation and/or decomposition usually were recorded just after fusion, thus preventing the determination of well-reproducible fusion peaks, this datum is rather rough and must be considered as a tentative one.

No mention was found in previous literature of the solid-to-solid phase transition detected in diethylammonium chloride. Only Wagner (1907) provided a qualitative observation of the polymorphic behavior of $(C_2H_5)_2NH_2Cl$, describing the difference in habit between the crystals obtained by crystallization from ethanolic solutions and those produced on cooling the melt. The occurrence of this phase change can be considered in good agreement with the existence of two transitions in solid (DEA)Cl under pressure, according to a paper by Hamann (1975). Other phase changes occurring in component B in the solid state, below the eutectic temperature of the binary mixtures, were neglected in this work.

The thermal properties of the molten mixtures can be discussed taking into account the fact that they are formed by incorporating the ionic species of the solute into the quasi-lattice structure of the solvent. With increasing solute concentration, the quasi-lattice of the solvent changes into that of the solute at the other end of the mole fraction scale and the nonideal behavior of the intermediate compositions can be observed. Figure 2 illustrates the molar volume, molar conductivity, and viscosity values for the given mixtures of the system at 473 K.

In the upper part of the plot, the molar volume V_{AB} vs the mole fraction of $(C_2H_5)_2NH_2Cl$ is shown. V_{AB} is given by the ratio

$$V_{AB} = M_{AB}/\rho_{AB} \tag{1}$$

where $M_{AB} = x_A M_A + x_B M_B$ is the mean molar mass of the mixture, M_A and M_B being the molar masses of (EA)Cl and (DEA)Cl, respectively, and ρ_{AB} is the density of the mixture. Nearly in the whole composition range the experimental molar volumes exhibit small negative deviations from

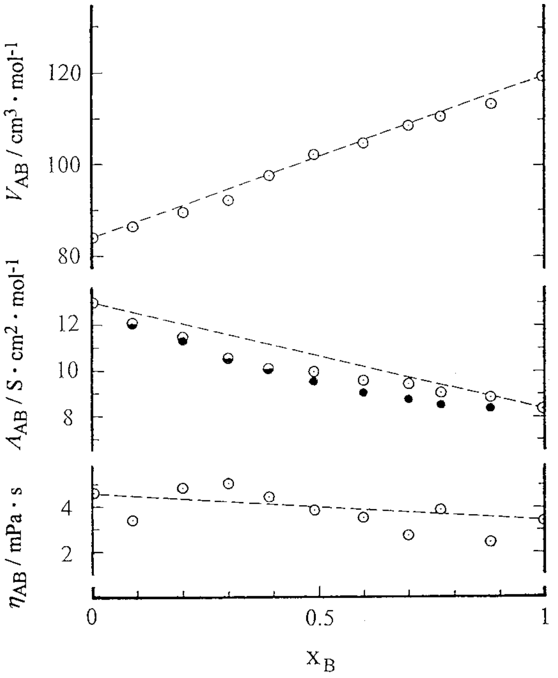

Figure 2. Transport properties of the system (EA)Cl−(DEA)Cl at 473 K; the dashed lines correspond to ideal behavior. Upper part: (○) molar volumes. Central part: (○) experimental molar conductivities; (●) molar conductivities calculated with Markov-Sumina's equation. Lower part: (○) experimental viscosities. The data of V_{AB} for x_B = 0.88 and 1.00 were obtained by linear extrapolation. The values of Λ_{AB} for x_B = 0.09 and 1.00; η_{AB} for x_B = 0.09, 0.20, 0.88, and 1.00 were obtained by extrapolation with Arrhenius equations.

Table 4. Experimental Viscosities ($\eta_{AB} \pm 0.5$) × 10^3/Pa·s of Molten $C_2H_5NH_3Cl$ (A) + $(C_2H_5)_2NH_2Cl$ (B) Mixtures at Selected Temperatures

	x_B										
T/K	0.00	0.09	0.20	0.30	0.39	0.49	0.60	0.70	0.77	0.88	1.00
393	16.0										
403	13.3										
413	10.9										
423	9.3		10.8								
428		7.9	9.8								
433	8.0	7.0	9.1								
438		6.5	8.3	8.8	8.1						
443	6.7	5.7	7.4	8.0	7.3						
448		5.2	6.9	7.4	6.8	6.3	5.9				
453	5.9	4.7	6.3	6.7	6.1	5.7	5.0				
458		4.2	5.7	6.2	5.7	5.1	4.6	3.6			
463	5.2	3.9	5.4	5.7	5.2	4.7	4.1	3.2			
468			4.9	5.4	4.8	4.3	3.8	3.0			
473	4.6			5.1	4.4	3.9	3.5	2.7	3.9		
478				4.8		3.5	3.2	2.6	3.4		
483	4.3							2.4	3.1	2.9	
488									2.7	2.8	
493	3.9								2.5	2.6	
498									2.4	2.5	
503											2.4
508											2.2
513											2.1
518											2.0
523											1.9

additivity. In the pure components, the Coulombic interactions of the alkylammonium cations with the chloride anions should be equal, whereas in the molten mixtures the electrostatic interactions of the anions with the smaller EA^+ cations are stronger than those with the larger DEA^+ ones.

The slight volume contraction observed on the macroscopic scale in the present system was also previously brought out in the mixtures of methylammonium chloride (MA)Cl with ethylammonium chloride (Zabinska et al., 1991). For the latter system at 473 K the molar volume decreases from the value of 84 cm^3·mol^{-1} [pure (EA)Cl] to 65 cm^3·mol^{-1} [pure (MA)Cl], whereas in the present case the molar volume increases to 120 cm^3·mol^{-1} for pure (DEA)Cl at the same temperature.

As for the experimental values of the molar conductivities at 473 K, they decrease smoothly from the higher conductivity of (EA)Cl (about 13 S·cm^2·mol^{-1}) to the lower one of (DEA)Cl (about 8 S·cm^2·mol^{-1}) and exhibit negative deviations from the simple additivity. In the central part of Figure 2 these deviations are compared with the dashed line of the additivity and the negative trend predicted by the Markov−Sumina equation (Markov and Sumina, 1956)-where $\lambda_B < \lambda_A$.

$$\lambda_{AB} = x^2_A\lambda_A + x^2_B\lambda_B + 2x_Ax_B\lambda_B \tag{2}$$

Departures from the trend indicated by eq 2 in the mixtures rich in (DEA)Cl may be caused by the fact that by increasing the concentration of this component, the associated structure created by (EA)Cl can be destroyed.

A similar behavior, but in the opposite sense, was observed in the mixtures of (EA)Cl + (MA)Cl (Zabinska et al., 1991) where by substituting EA^+ with MA^+ the molar conductivity increases to about 24 S·cm^2·mol^{-1} and the system exhibits positive deviations from the simple additivity. The hydrogen cations dissolved in these melts as a result of the acidic dissociation of the alkylammonium cations may actually play a considerable role in the transport of electric charge.

On the other hand, the viscous flow should not be significantly influenced by the presence of protons in the melt. In the two binary systems under discussion, interesting experimental evidence of this fact can be found by comparing the viscosities of the pure components determined in the same temperature range: the values for (DEA)Cl (Table 4 in this work) are close to those of pure (MA)Cl [Table 2 in the quoted paper (Zabinska et al., 1991)]. In the lower part of Figure 2, the experimental data of viscosities are illustrated. In both systems, viscosities decrease slightly from about 5 Pa·s [pure (EA)Cl] to about 3 Pa·s for both pure (DEA)Cl and (MA)Cl. Owing to the different procedures of carrying out conductivity and viscosity measurements, the viscosity data obtained for both systems show relatively large fluctuations in the whole composition range, if compared with the conductivity data.

From the above-mentioned data of conductivity and viscosity, the Walden product (Walden and Birr, 1931) was obtained. It is decreasing with increasing concentration of (DEA)Cl as shown in Figure 3. The relatively large fluctuations of the Walden product reflect the combined experimental uncertainties, especially those of the viscosity data.

For the temperature dependence of conductivity and viscosity, a behavior of the Arrhenius type is observed. The activation energies for the conductivity and the viscous flow can be obtained from the following equations:

$$\ln \lambda = \ln A_\lambda + \frac{-E_\lambda}{RT} \tag{3a}$$

$$\ln \eta = \ln A_\eta + \frac{E_\eta}{RT} \tag{3b}$$

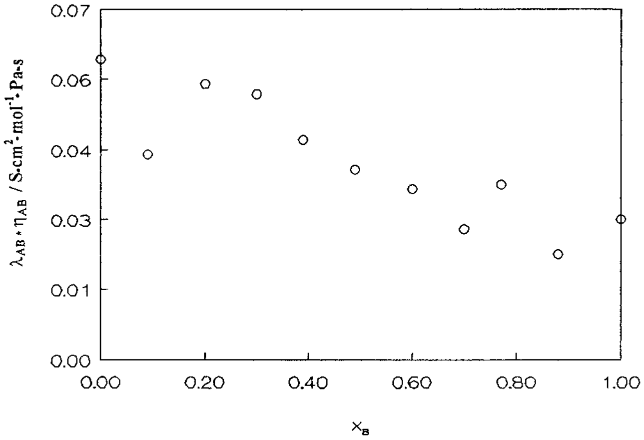

Figure 3. Plot of the Walden product as a function of x_B at 473 K.

Table 5. Linear Regression Coefficients for ln λ According to Equation 3a as a Function of x_B

x_B	ln A_λ	$-E_\lambda$/kJ mol^{-1}	*R*, coefficient of correlation
0.00	6.72 ± 0.08	16.3 ± 0.3	0.9987
0.09	6.65 ± 0.06	16.3 ± 0.2	0.9996
0.20	6.83 ± 0.08	17.2 ± 0.3	0.9993
0.30	6.87 ± 0.08	17.7 ± 0.3	0.9996
0.39	6.80 ± 0.09	17.4 ± 0.3	0.9990
0.49	7.07 ± 0.06	18.6 ± 0.2	0.9986
0.60	6.94 ± 0.04	18.4 ± 0.1	0.9990
0.70	7.01 ± 0.19	18.9 ± 0.8	0.9966
0.77	6.62 ± 0.03	17.4 ± 0.1	0.9995
0.88	6.03 ± 0.07	15.1 ± 0.3	0.9990
1.00	6.13 ± 0.19	15.7 ± 0.8	0.9941

Table 6. Linear Regression Coefficients for ln η According to Equation 3b as a Function of x_B

x_B	$-$ln A_η	E_η/kJ mol^{-1}	*R*, coefficient of correlation
0.00	11.23 ± 0.12	22.1 ± 0.5	0.9665
0.09	14.26 ± 0.12	33.5 ± 0.4	0.9924
0.20	12.81 ± 0.10	29.1 ± 0.4	0.9963
0.30	12.08 ± 0.16	26.7 ± 0.6	0.9938
0.39	12.93 ± 0.10	29.5 ± 0.4	0.9942
0.49	14.32 ± 0.15	34.4 ± 0.6	0.9940
0.60	14.39 ± 0.37	34.3 ± 1.4	0.9948
0.70	13.44 ± 0.44	29.7 ± 1.4	0.9972
0.77	15.43 ± 0.60	39.2 ± 2.4	0.9962
0.88	11.60 ± 0.17	23.3 ± 0.7	0.9995
1.00	11.14 ± 0.13	21.3 ± 0.5	0.9992

In Tables 5 and 6 the activation energies for the conductivity and the viscous flow as determined from the eqs 3a and 3b, respectively, are reported.

The temperature dependence of the specific electrical conductivity can be well-described by the following polynomial of the second order, as suggested by Easteal and Hodge (1970)

$$k_{AB}/\mathrm{S{\cdot}cm^{-1}} = a_0 + a_1 T/\mathrm{K} + a_2 (T/\mathrm{K})^2 \qquad (4)$$

The computer-fitted parameters are reported in Table 7.

Thus, in the present system it seems that the conductivities of the binary mixtures follow the same general trend as those of the pure salts, i.e., the richer the compositions are in the larger alkyl group, the less conductive the mixtures become.

Table 7. Conductivity Constants Calculated According to Equation 4 as a Function of x_B

x_B	a_0	a_1	a_2	standard deviation	*R*, coeffcient of correlation
0.00	0.0174	−0.512	1.850	0.025	0.9994
0.09	0.3691	1.144	0.147	0.018	0.9997
0.20	0.4495	1.483	−0.555	0.020	0.9992
0.30	0.3879	1.242	−0.383	0.023	0.9997
0.39	0.1275	0.059	0.923	0.023	0.9997
0.49	0.1459	0.172	0.720	0.029	0.9998
0.60	0.0982	−0.026	0.901	0.025	0.9999
0.70	0.6780	2.397	−1.649	0.019	0.9999
0.77	0.1289	0.151	0.623	0.015	0.9998
0.88	0.6435	2.306	1.654	0.009	0.9989
1.00	1.0148	−4.241	4.771	0.006	0.9950

Conclusions

Data of transport properties were measured on the pure components and nine mixtures of $C_2H_5NH_3Cl$ + $(C_2H_5)_2NH_2Cl$. The liquidus curves of the system were determined with thermal methods.

(EA)Cl and (DEA)Cl were chosen for the differences in size and shape of their substituted ammonium cations. The longest estimated distance between the hydrogen atoms in the diethylammonium ion is about 6.6 Å, i.e., by $^1/_3$ larger than that in the ethylammonium one, where it is ~4.2 Å. As a result of the interactions of these different ions with the chloride anions, the nonadditive behavior of these molten mixtures has been brought out.

Conductivity decreases continuously from the higher value of (EA)Cl to the lower one of (DEA)Cl, showing negative deviations from the additivity as a function of the mole fraction over the whole composition range. The existence in the molten phase of H^+ ions as a result of the dissociation of both cations, and the possible formation of weak hydrogen bonds, might also play a role in this behavior of conductivity.

Because of the rather large fluctuations of the experimental measurements, the viscosity values show large uncertainties. However, it may be remarked that the (EA)Cl + (DEA)Cl system and the previously examined (MEA)Cl + (EA)Cl one show a similar behavior.

Conductivities and viscosities display an Arrhenius behavior, and the energies of these activation processes can be evaluated on the basis of an Arrhenius-type equation.

Registry No. Supplied by Authors: $C_2H_5NH_3Cl$, [557-66-4]; $(C_2H_5)_2NH_2Cl$, [660-68-4].

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