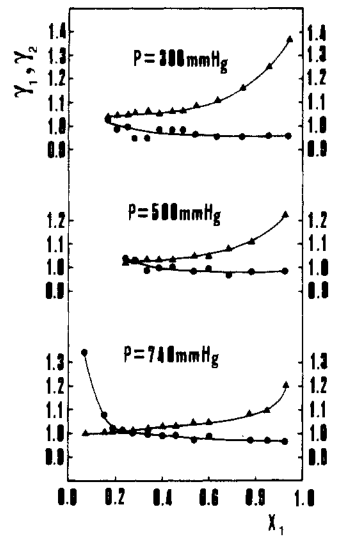

Figure 1. Experimental activity coefficients of the system 1,3-dioxolane (1)-acetone (2) at P = 300, 500, and 740 mmHg: (▲, ●) experimental values, (—) graphical smoothing.

Table IV. Standard Deviation σ and Average Deviation $\Delta\gamma$ between Experimental and Calculated Activity Coefficients for 1,3-Dioxolane (1)-Acetone (2)

	NRTL eq		
press./mmHg	σ^a	$\Delta\gamma_1{}^b$	$\Delta\gamma_2{}^b$
300	0.9	0.07	0.06
500	1.5	0.04	0.02
740	2.1	0.03	0.04

[a] $\sigma(\text{mmHg}) = [\sum^n (P_{k,\text{exptl}} - P_{k,\text{calcd}})^2/(n - n_p)]^{1/2}$. n_p = number of adjustable parameters. [b] $\Delta\gamma = \sum_{k=1}^{n} |\gamma_{k,\text{exptl}} - \gamma_{k,\text{calcd}}|/n$.

gether with their estimated standard errors. The objective function in the least-squares method is

$$\Phi = \sum_{k=1}^{n} (P_{k,\text{exptl}} - P_{k,\text{calcd}})^2 \qquad (7)$$

$$P_{\text{calcd}} = P^\circ_1 x_1 \gamma_1 + P^\circ_2 x_2 \gamma_2 \qquad (8)$$

where n is the number of experimental points and γ_1 and γ_2 are given by eq 3.

The uncertainty of the parameters is defined as the variation of the parameter giving rise to a variation of $\sigma_P{}^2$ (1 mmHg) for Φ at its minimum. In the calculations, a computer program, based on the algorithms of Nelder and Mead (*7*) and Fletcher (*8*), was used. In Table IV the root-mean-square deviation σ and the average deviations $\Delta\gamma$ between experimental and calculated activity coefficients γ_1 and γ_2 are shown. The activity coefficients γ_1 and γ_2 were also correlated by using the Wilson, LEMF, and Redlich-Kister equations.

Wilson and LEMF equations lead to values of σ slightly higher than the ones given in Table IV and values of $\Delta\gamma$ up to twice those of the NRTL equation. On the other hand, the minimization of the experimental data made with the Redlich-Kister equation with two temperature-dependent parameters gives rise to values of σ (σ = 1.0, 0.9, and 1.8 for the pressures of 300, 500, and 740, respectively) comparable with those obtained by using the NRTL equation, but leads to higher values of $\Delta\gamma_1$ and Δy_2 ($\Delta\gamma_1$ = 10%, 5%, and 4%; $\Delta\gamma_2$ = 6%, 2%, and 5% for the pressures of 300, 500, and 740 mmHg, respectively). For this reason only the parameters of the NRTL equation are shown in Table III.

Registry No. 1,3-Dioxolane, 646-06-0; acetone, 67-64-1.

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Conductance of Electrolytes in 1,2-Dichloro-1,1-difluoroethane

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Conductivities are presented for solutions of tetrabutylammonium tetrafluoroborate and tetrabutylphosphonium bromide in 1,2-dichloro-1,1-difluoroethane at 25 °C. For a given concentration, solutions of tetrabutylammonium salt were found to be more conductive than the tetrabutylphosphonium salt. Molar conductances display a distinct minimum at about 0.02 mol L^{-1}.

Introduction

The conductance of R_4ZX salt solutions, where R = alkyl group, and Z = N or P and X is an anion, has been widely studied (*1-5*). However, these same measurements employing halocarbons as the solvent are relatively rare. The present paper investigates the conductivity of such salts in 1,2-dichloro-1,1-difluoroethane for evaluation in an experimental battery.

Experimental Section

1,2-Dichloro-1,1-difluoroethane (obtained from PCR Research Chemicals, Inc.) was dried over molecular sieves for 12 h prior to distillation under nitrogen. Only the middle fraction (bp 47 °C) was retained.

Tetrabutylammonium tetrafluoroborate and tetrabutylphosphonium bromide obtained from Aldrich Chemical Co. were purified by recrystallization from a mixture of ethyl acetate and diethyl ether. Both salts were vacuum dried at 60-70 °C for 48 h. Due to the hygroscopic nature of these salts, extreme care was taken to avoid contact of these salts with water va-

Table I. Conductance of NBu_4BF_4 Solutions in 1,2-Dichloro-1,1-difluoroethane at 25 °C

	conductance			conductance	
C,[a] mol L^{-1}	$10^{-3}\kappa$,[b] Ω^{-1} cm^{-1}	Λ,[c] Ω^{-1} cm^2 mol^{-1}	C,[a] mol L^{-1}	$10^{-3}\kappa$,[b] Ω^{-1} cm^{-1}	Λ,[c] Ω^{-1} cm^2 mol^{-1}
2.00	1.24	0.620	0.300	1.69	5.63
1.80	1.73	0.963	0.250	1.45	5.81
1.60	2.18	1.36	0.200	1.16	5.82
1.43	2.58	1.81	0.120	0.673	5.61
1.25	2.98	2.38	0.0900	0.474	5.27
1.00	3.09	3.09	0.0514	0.257	5.00
0.800	3.04	3.80	0.0300	0.147	4.92
0.600	2.76	4.60	0.00960	0.0502	5.23
0.500	2.42	4.84	0.00384	0.0253	6.60
0.400	2.14	5.35	0.000960	0.00981	10.02

[a] Molar concentration. [b] Specific conductance. [c] Molar conductance.

Table II. Conductance of PBu_4Br Solutions in 1,2-Dichloro-1,1-difluoroethane at 25 °C

	conductance			conductance	
C,[a] mol L^{-1}	$10^{-3}\kappa$,[b] Ω^{-1} cm^{-1}	Λ,[c] Ω^{-1} cm^2 mol^{-1}	C,[a] mol L^{-1}	$10^{-3}\kappa$,[b] Ω^{-1} cm^{-1}	Λ,[c] Ω^{-1} cm^2 mol^{-1}
1.50	1.22	0.811	0.273	0.908	3.33
1.25	1.50	1.20	0.180	0.571	3.17
1.07	1.72	1.60	0.129	0.381	2.95
1.00	1.77	1.77	0.0900	0.0248	2.75
0.938	1.81	1.92	0.0720	0.186	2.59
0.750	1.80	2.40	0.0400	0.0864	2.16
0.643	1.72	2.67	0.0245	0.0404	1.65
0.562	1.60	2.86	0.00735	0.0133	1.81
0.500	1.49	2.98	0.00245	0.00534	2.18
0.375	1.23	3.28			

[a] Molar concentration. [b] Specific conductance. [c] Molar conductance.

por. All manipulations involving the tetrabutyl salts were carried out in a dry room in which the relative humidity did not exceed 0.4%.

Conductivity measurements were carried out with a Yellow Springs Instrument borosilicate dip-type cell (Model no. 3403) requiring 5 mL of sample. The platinum electrodes of this cell were platinized and the cell constant was determined as 1.09 cm^{-1}. All resistance measurements were carried out with a General Radio type 1650-B impedance bridge at 1000 Hz. Capacitance balance was provided to ensure sharp null points. The bridge measured resistance with an accuracy of ±1.0%. Solutions were maintained at 25 ± 0.2 °C by means of a Forma Scientific, Inc., Model 2095-2 constant-temperature bath. Equilibrium temperature of the bath was read on a mercury thermometer (traceable to NBS) with an accuracy of ±0.1 °C. The dielectric constant and the dissipation factor of 1,2-dichloro-1,1-difluoroethane were measured by Dr. L. Mandelcorn (Westinghouse Electric Corp.) in a three-terminal Balsbaugh cell with an ESI 707B capacitance bridge after absorbing ionic impurities with fuller's earth.

Viscosity measurements were made (by L. Mandelcorn) with a Cannon-Fenske viscometer (tube constant = 2.067×10^{-13} cSt s^{-1} at 100 °F) according to ASTM D445 procedure.

Results

The measured molar conductances, specific conductances, and the corresponding electrolyte concentrations (M) are given in Table I for NBu_4BF_4 and Table II for PBu_4Br. The resistivity of the pure solvent, 1,2-dichloro-1,1-difluoroethane, was found to be 3.6×10^6 Ω cm.

The viscosity of the pure solvent was found to be 0.374 cSt, standard deviation 0.001 cSt at 24 °C. Its dielectric constant and dissipation factor (tan δ) at 25 °C were measured as 8.4 and 3×10^{-2}, respectively, at 60 Hz and 8.4 and 3×10^{-3} at 1000 Hz.

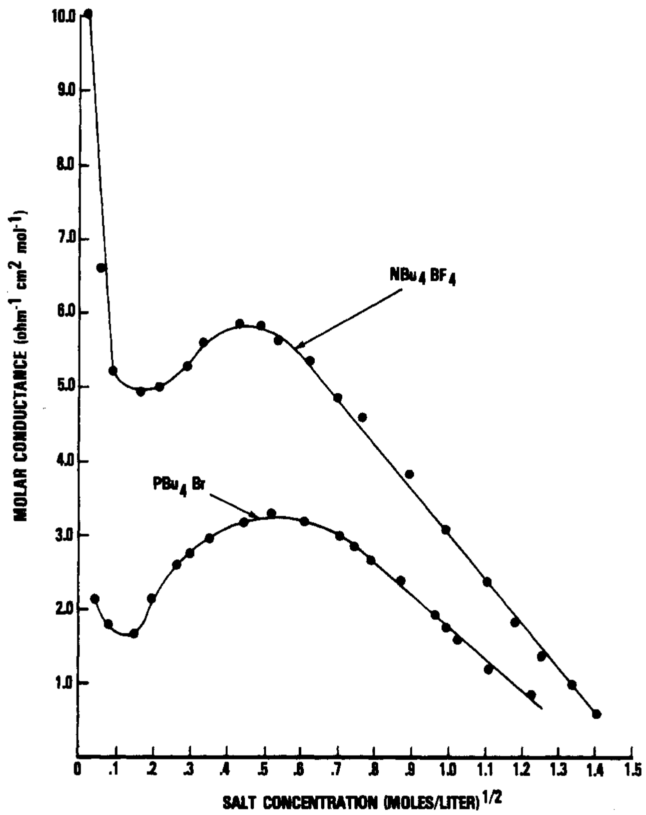

Figure 1. Molar conductance of salt in 1,2-dichloro-1,1-difluoroethane at 25 °C.

The behavior of molar conductance (Λ) vs. the square root of the salt concentration is consonant with regarding these solutions as associated strong electrolytes (*6*). Minima in Λ at low concentrations such as appear in Figure 1 have been observed in solvents with sufficiently low dielectric constant ($\epsilon < 12$) (*7*). After the minimum, the conductance increases with concentration until a maximum is reached around 0.4–0.5 $(mol/L)^{1/2}$. This behavior is indicative of the formation of highly associated ion clusters which may include ion pairs, triple ions, or more complex ion aggregates (*8–10*). For example, the rise in conductance after the minimum is attributed to the conversion of nonconducting ion pairs to conductive triple ions (*8*). The fall in conductance at high concentrations may relate to the formation of nonconducting quadruple ions or to the increasing solution viscosity that was qualitatively observed in this region.

Acknowledgment

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Registry No. NBu_4BF_4, 429-42-5; PBu_4Br, 3115-68-2.

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