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Speed of Sound, Densities, and Viscosities for Solutions of Lithium Hexafluoroarsenate in Tetrahydrofuran at 283.15, 298.15, and 313.15 K

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Speed of sound, viscosity, and density have been measured for solutions of $LiAsF_6$ in tetrahydrofuran over a wide range of concentrations at temperatures from 283.15 K to 313.15 K.

Introduction

The volumetric properties of solutions and their dependence on temperature and pressure and the viscosities, particularly at high concentrations, are used in designing chemical power sources with liquid phase electrolytes. These properties together with electrochemical stability, electrode potential, and electrical conductivity are the basis for predicting the behavior of electrolytes as chemical power sources.

The analysis of densities, viscosities, and speed of sound can be used to infer interrelations between the state of ion−molecular forms in solution and the transfer processes. Of interest are solutions with low relative permittivity ϵ. The systems studied are characterized by complex association and solvation processes, which make the behavior of these systems difficult to predict.

Experimental Section

Materials. Synthesized lithium hexafluoroarsenate of high purity (>99.2%) was used in this investigation. Reagent grade tetrahydrofuran (purity 99.5%) was dried with molecular sieves and distilled under an atmosphere of argon. The water content found by the Karl Fischer method (Mitchell and Smith, 1976) in the solution was less than 0.005%.

Apparatus and Procedures. Measurements of density (ρ) were carried out with an A. Paar vibrating densimeter (DMA-602) with an error less than ± 0.01 kg/m^3. To ensure this accuracy, the temperature was contrrolled to within 0.002 K.

The speed of sound (U) was measured with a specially designed laser interferometer (6 MHz) of variable path length with a percentage accuracy (2 to 5) $\times 10^{-3}$%. The accuracy of the apparatus was tested using high-purity water (Del Grosso and Mader, 1972). The interferometer was found to measure ultrasonic speeds at 6, 18, and 30 MHz with an error of less than 0.001%. The analysis showed that fluctuations in the sample temperature during the rod motion bring about the maximum error in the measurements of the speed of sound. The above accuracy requires temperatures of both the cell and the rod with a reflector to be maintained within ± 0.005 K. Figure 1 shows a schematic diagram of the laser ultrasound interferometer with variable path length designed by Voleigis (Voleigis and Jaronis, 1973).

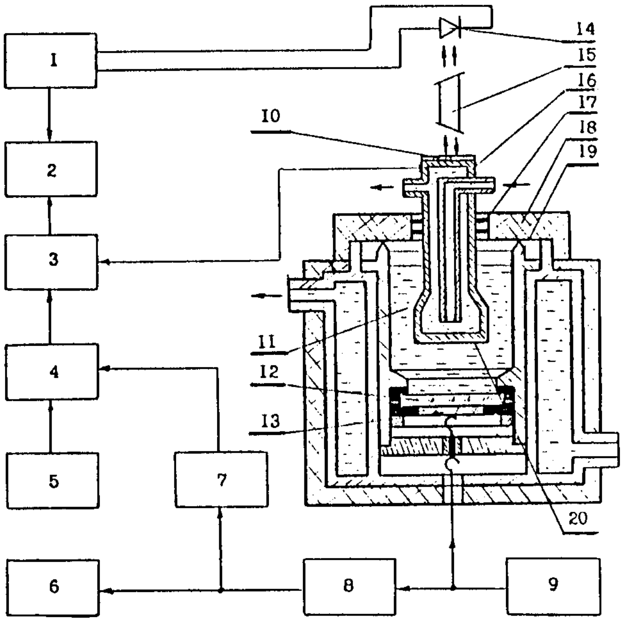

Figure 1. Schematic diagram of the laser ultrasound interferometer: (1) generator of the displacement marks, (2) marks counter, (3) trigger of counting, (4) counter of half-wave number, (5) controller of the number of half-waves, (6) oscillograph, (7) resonance peak detector, (8) detector, (9) high-frequency generator, (10) reflector of the laser radiation, (11) liquid under study, (12) quartz membrane, (13) quartz emitter, (14) photodiode, (15) laser, (16) rod, (17) gland, (18) cover, (19) cell, (20) reflector of the ultrasound.

Kinematic viscosity was determined with a hanging level capillary viscosimeter (Davydova et al., 1985), adapted for operation under vacuum and having a photoelectron detection system. Double thermostatic control, the first circuit of which includes a cryostat MK-70, maintained the temperature to ± 0.004 K. The maximum error in the value of η was 0.3%. From the measurements, the molar volumes (V_m), coefficients of volumetric expansion (α), apparent molar volumes ($V_{2,\varphi}$), isentropic compressibilities (k_s), and dynamic viscosity (η) were calculated from eqs 1−4, respectively.

$$V_m = \frac{M_1(1 + mM_2)}{\rho(1 + mM_1)} \tag{1}$$

$$V_{2,\varphi} = \frac{(\rho_o - \rho)}{\rho_o \rho m} + \frac{M_2}{\rho} \tag{2}$$

$$\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P = -\frac{1}{\rho}\left(\frac{\partial \rho}{\partial T}\right)_P \tag{3}$$

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Table 1. Densities (ρ), Molar Volumes (V_m), Coefficients of Thermal Expansion (α), and Isentropic Compressibilities (k_s) of $LiAsF_6$ Solutions in Tetrahydrofuran

$100m$/ mol·kg^{-1}	ρ/ kg·m^{-3}	10^6V_m/ m^3·mol^{-1}	$10^{10}k_s$/ Pa^{-1}	$10^3\alpha$/ K^{-1}
		T = 283.15 K		
0	898.37	80.28	6.097	1.204
0.988	899.70	80.26	6.092	1.203
2.038	901.25	80.22	6.083	1.199
3.121	902.83	80.19	6.073	1.199
5.017	905.60	80.13	6.056	1.196
6.372	907.58	80.09	6.044	1.194
8.076	910.08	80.03	6.028	1.191
9.778	912.35	80.00	6.014	1.188
11.79	915.22	79.94	5.996	1.187
15.33	920.24	79.84	5.964	1.179
23.86	932.39	79.60	5.886	1.166
31.86	943.69	79.37	5.814	1.154
40.30	955.49	79.14	5.738	1.142
52.26	972.30	78.80	5.630	1.125
60.84	983.85	78.59	5.555	1.115
74.24	1001.80	78.27	5.439	1.099
90.13	1023.00	77.88	5.301	1.081
108.32	1046.50	77.48	5.147	1.062
126.22	1069.40	77.09	4.997	1.045
		T = 298.15 K		
0	882.08	81.76	6.942	1.247
1.854	884.64	81.71	6.927	1.245
3.488	887.14	81.65	6.909	1.242
3.993	887.84	81.63	6.904	1.241
5.012	889.36	81.59	6.893	1.240
7.206	892.51	81.52	6.869	1.237
7.915	893.46	81.51	6.862	1.236
8.860	894.87	81.47	6.851	1.235
32.45	927.97	80.77	6.583	1.199
50.99	953.78	80.22	6.380	1.168
74.79	986.13	79.56	6.130	1.125
95.20	1013.12	79.03	5.916	1.085
129.02	1055.93	78.28	5.590	1.015
		T = 313.15 K		
0	865.44	83.33	7.950	1.292
1.009	866.78	83.31	7.938	1.291
3.779	870.64	83.22	7.904	1.288
5.861	873.55	83.16	7.876	1.286
8.894	877.74	83.06	7.836	1.283
10.90	880.93	82.96	7.806	1.280
16.83	889.27	82.27	7.726	1.272
37.11	917.89	82.09	7.446	1.238
56.78	944.80	81.49	7.185	1.198
70.56	963.37	81.08	7.007	1.165
84.84	982.59	80.66	6.821	1.126
94.59	995.82	80.36	6.696	1.098

Table 2. Coefficients A_i of Equation 9 and Standard Deviation of Fit (σ)

T/K	A_1	A_2	$-A_3$	100σ/kg·m^{-3}
283.15	142.98	4.53	10.01	8.3
298.15	142.56	4.90	10.34	9.7
313.15	139.84	7.27	9.78	15.1

$$k_s = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_S = (U^2\rho)^{-1} \qquad (4)$$

Results and Discussion

The analysis of the volumetric properties indicates that the volumetric expansion coefficient (Table 1) decreases in magnitude almost linearly with an increase in electrolyte concentration m. The density values were well fitted to the polynomial

$$\Delta\rho = A_1m + A_2m^{1.5} + A_3m^2 \qquad (5)$$

The coefficients are given in Table 2.

Table 3. Speeds of Sound (U) and Dynamic Viscosities (η) for $LiAsF_6$ Solutions in Tetrahydrofuran

$100m$/ mol·kg^{-1}	U/ m·s^{-1}	10η/ mPa·s	$100m$/ mol·kg^{-1}	U/ m·s^{-1}	10η/ mPa·s
		T = 283.15 K			
0	1351.17	5.50	23.86	1349.83	6.77
0.988	1350.78	5.54	31.86	1350.06	7.26
2.038	1350.62	5.59	40.30	1350.55	7.81
3.121	1350.48	5.64	52.26	1351.63	8.67
5.017	1350.30	5.74	60.84	1352.68	9.35
6.372	1350.20	5.81	74.24	1354.78	10.51
8.076	1350.09	5.89	90.13	1357.95	12.08
9.778	1350.01	5.98	108.32	1362.52	14.16
11.79	1349.93	6.09	126.22	1367.96	16.55
15.33	1349.83	6.28			
		T = 298.15 K			
0	1277.90	4.68	8.860	1277.16	5.01
1.854	1277.48	4.73	32.45	1279.46	6.11
3.488	1277.31	4.79	50.99	1281.96	7.14
3.993	1277.28	4.81	74.79	1286.19	8.71
5.012	1277.22	4.85	95.20	1291.64	10.34
7.206	1277.15	4.94	129.02	1301.65	13.73
7.915	1277.15	4.97			
		T = 313.15 K			
0	1205.59	4.03	16.83	1206.43	4.63
1.009	1205.59	4.07	37.11	1209.62	5.46
3.779	1205.47	4.16	56.78	1213.72	6.41
5.861	1205.57	4.23	70.56	1217.10	7.17
8.894	1205.75	4.34	84.84	1221.52	8.06
10.90	1205.90	4.41	94.59	1224.64	8.73

The apparent molar volumes of the electrolytes at infinite dilution have been obtained. These values are 40.5 × 10^{-6} m^3/mol, 37.7 × 10^{-6} m^3/mol, and 36.8 × 10^{-6} m^3/mol at 283.15 K, 298.15 K, and 313.15 K, respectively. The association constant of $LiAsF_6$ in tetrahydrofuran has an order of magnitude of (10^4 or 10^5) L/mol (Afanasyev and Korolev, 1992). Strong association is indicated by a minimum in the dependence of conductivity on concentration, which lies in the range of rather low concentrations (0.01 mol/L). Therefore, the molar volumes of the electrolyte extrapolated to infinite dilution correspond, apparently, to the partial molar volumes of the ion pairs. The molar electrolyte volume, calculated from the crystalline phase density of $LiAsF_6$, is 72.3 × 10^{-6} m^3/mol. The considerable difference between the partial molar volume ($V^0_{2,\varphi} = \bar{V}^0_2$) and the volume of the electrolyte itself suggests strong electrolyte−solvent interaction. It is due to the fact that tetrahydrofuran interacts with Li^+ by the donor−acceptor mechanism. At the same time, low relative permittivity of the solvent favors the transfer of charge at long distances and strengthens the effects of polarization. The pseudo molar volume decreases gradually with the increase in the electrolyte concentration and decrease in temperature.

The density and acoustic measurements (Table 3) enabled us to estimate the derivative of molar volume in respect to pressure and calculate the isentropic compressibility (Figure 2). The latter appeared to be a linear function of the solute molar fraction ($R > 0.9999$). As a whole, the investigation of volumetric properties showed that the molar volume and its relative changes with temperature (α) and pressure (k_s) are monotonic in the whole studied range of concentration and temperature.

The dependence of the speed of sound on concentration displays a characteristic minimum at $X_2 < 0.03$ shifting to the region of lower concentrations at increasing temperature. One can suggest that the minimum is attributed to the presence of residual water in tetrahydrofuran. However, investigations on water influence established that the change in water concentration leads only to the change in

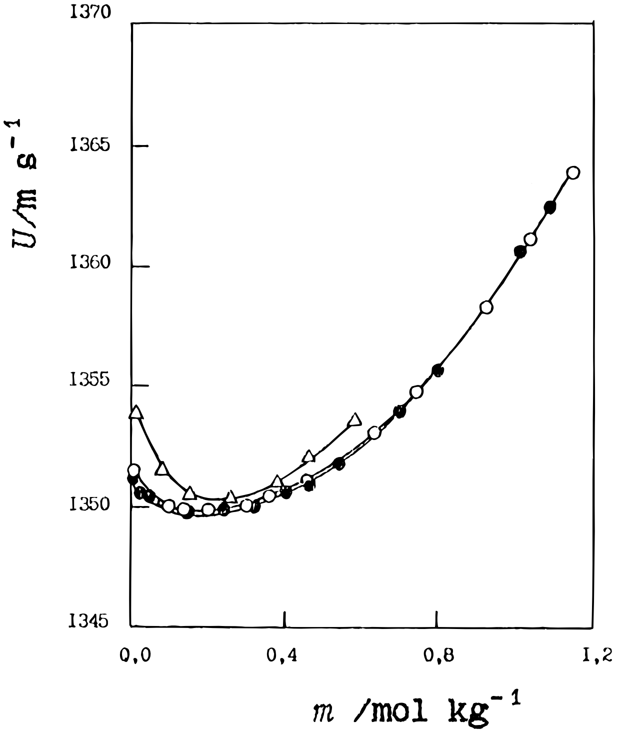

Figure 2. Ultrasound speed (U) as a function of the concentration (m) of $\mathrm{LiAsF_6}$ in tetrahydrofuran containing small amounts of water: (△) 0.0137%; (○) 0.097%; (●) 0.85% at 283.15 K.

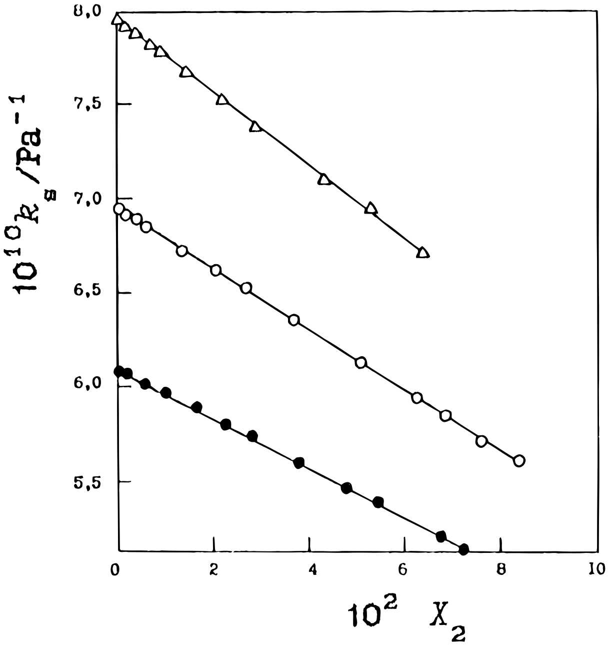

Figure 3. Isentropic compessibility (k_s) as a function of the mole fraction (X_2) of $\mathrm{LiAsF_6}$ in tetrahydrofuran: (●) 283.15 K; (○) 298.15 K; (△) 313.15 K.

the magnitude of U, that of the minimum being unchanged (Figure 3). Such a dependency is, apparently, due to the peculiarities of the binary system itself. Equation 4 relates the speed of sound to the value of ρk_s. As the first multiple in this product increases and the second one decreases with increasing electrolyte concentration, then the dependence $U = f(m)$ can be extreme.

Solvation numbers of $\mathrm{LiAsF_6}$ in tetrahydrofuran at different temperatures were estimated by the speed of sound measurements. Upon formation of incompressible regions at solvation the following equation (Marcus, 1985) is applicable:

$$\lim_{m\to 0} K_{2,\varphi} = h\bar{V}_1^0 k_1^0 \qquad (6)$$

where $K_{2,\varphi}$ is the apparent molal compressibility, h is the number of solvent moles in the incompressible region, and $\bar{V}_1^0$ and k_1^0 are the partial molar volume and compressibility of solvent, respectively. The functions $(\partial V/\partial P)_{S,T} = Vk = f(m)$ proved to be linear in a wide range of concentrations (up to 1 mol·L $^{-1}$) at all the temperatures studied. The solvation numbers obtained are weakly dependent on concentration. These values are $h_{283.15} = 1.67$, $h_{298.15} = 1.84$, and $h_{313.15} = 2.05$. At increasing temperature the electrolyte–solvent interaction gets stronger, which is also proved by the decrease in the partial molar volume of the salt.

Viscosimetry investigations indicate complex solvation–association interactions in the system $\mathrm{LiAsF_6}$ + tetrahydrofuran. A steep increase in dynamic viscosity (Table 3) in the range of high concentrations (>0.2 mol·L $^{-1}$) causes a deviation from the Jones–Dole (1929) law, indicating a process of intermolecular association. The isotherms of dynamic viscosity in the whole studied range of concentrations behave exponentially:

$$\eta = \eta_0 \mathrm{e}^{Bm} \qquad (7)$$

Such a dependence is typical for solutions of electrolytes in aprotic solvents with low and medium dielectric constants and is a particular case of the Einstein–Vand–Stocks (Vand, 1948) equation. For the solutions of $\mathrm{LiAsF_6}$ in tetrahydrofuran we have

$$T = 283.15\ \mathrm{K},\ \ln(\eta/\mathrm{mP{\cdot}s}) = 0.8739(m/\mathrm{mol{\cdot}kg}) - 0.5991,\ (\sigma/\mathrm{mP{\cdot}s}) = 0.0003$$

$$T = 298.15\ \mathrm{K},\ \ln(\eta/\mathrm{mP{\cdot}s}) = 0.8387(m/\mathrm{mol{\cdot}kg}) - 0.7651,\ (\sigma/\mathrm{mP{\cdot}s}) = 0.0007$$

$$T = 313.15\ \mathrm{K},\ \ln(\eta/\mathrm{mP{\cdot}s}) = 0.8159(m/\mathrm{mol{\cdot}kg}) - 0.9075,\ (\sigma/\mathrm{mP{\cdot}s}) = 0.0008$$

The values of B were determined for the region of the Jones–Dole equation validity. They are 1.06 L/mol at 283.15 K, 1.00 L/mol at 298.15 K, and 0.92 L/mol at 313.15 K. Large positive values of these coefficients indicate the big size of moving particles, decreasing with increasing temperature. These phenomena can be attributed to the breakup of the solvation shell due to the thermal motion.

This study suggests that there are several coexisting equilibria in solutions of $\mathrm{LiAsF_6}$ in solvents with low relative permittivity:

$$\mathrm{Li}^{+}_{\mathrm{sol}} + \mathrm{AsF_6}{}^{-}_{\mathrm{sol}} \overset{K_1}{=} \mathrm{LiAsF}_{6\ \mathrm{sol}} \qquad (8)$$

$$2\mathrm{LiAsF}_{6\ \mathrm{sol}} \overset{K_2}{=} (\mathrm{LiAsF_6})_{2\ \mathrm{sol}} \quad \text{and further aggregation} \qquad (9)$$

$$2\mathrm{LiAsF}_{6\ \mathrm{sol}} \overset{K_3}{=} \mathrm{AsF_6}{}^{-}_{\mathrm{sol}} + \mathrm{Li_2\,AsF_6}{}^{+}_{\mathrm{sol}} \qquad (10)$$

The first equilibrium is considerably shifted to the right ($K_1 = 10^4–10^5$); the second one manifests at increasing concentrations, and K_2 has an order of magnitude 10 (as in methyl acetate (Salomon et al., 1989)). Comparing the constants K_1 and K_2, one can expect that even in the range of diluted solutions, the molecular form of the electrolyte will be an associated one. The third equilibrium provides a relatively high electrical conductivity at high concentrations of the electrolyte, which to a large extent is determined by the electrostatic characteristics of the molecular forms of ionoform, taking part in solvation. At the same time, the system considered is characterized by a strong solvation interaction by the donor−acceptor mechanism.

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