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Electrolyte Conductivity of NaSCN in Propan-1-ol and Propan-2-ol Solutions at Temperatures from 228 K to 298 K

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Conductivity measurements of sodium thiocyanate solutions in propan-1-ol and propan-2-ol in the concentration range from (0.0001 to 0.004) mol·kg^{-1} from 228.15 K to 298.15 K have been performed with high precision. Data analysis has been performed on the basis of the chemical model (CM) of electrolyte solutions including short-range interactions.

Introduction

In this paper we report measurements of the conductivity of highly dilute NaSCN solutions in propan-1-ol and propan-2-ol (0.0001 to 0.004 mol·kg^{-1}) at 10 K intervals from 228.15 K to 298.15 K. The measurements were made using equipment known to yield precise data required for the determination of the limiting conductivity Λ^∞, the association constant K_A, the ion distance parameters, and the contributions of interaction forces in the solutions as a function of temperature and electrolyte concentration. Data analysis was carried out with the conductivity equation of the low-concentration Chemical Model (lcCM).[1]

Data from conductivity measurements over wide temperature ranges subjected to an analysis at the lcCM level are a most convenient and efficient source for the determination of the structural features of an electrolyte solution. Conductivity studies on NaSCN in propan-1-ol[2] and propan-2-ol[3] were executed up to now only at 298.15 K. A comprehensive temperature-dependent conductivity study has been performed in our laboratory on KSCN in propan-1-ol.[4]

Experimental Section

Materials. Propan-1-ol and propan-2-ol (both Merck, p.a.) were dried with amalgamated aluminum shot,[5] and ammonia and amines were removed by boiling for 12 h in the presence of sulfanilic acid. Subsequent distillation over a packed column of the type presented in the literature[6] reduced the water content to <10 ppm (determined by Karl Fischer titration). No impurities were found by gas chromatography. The specific conductivity of the product was $<10^{-9}$ S·cm^{-1}.

Sodium thiocyanate, NaSCN (Sigma, ACS Reagent, 540-72-7) was dried at 90 °C and $p < 10^{-2}$ mbar in the presence of P_2O_5.

Potassium chloride, used in aqueous solutions for cell calibration, was recrystallized from highly purified water and dried at 300 °C and $p < 1$ Pa in the presence of P_2O_5.

All operations and the final storage of the purified products were carried out under pure nitrogen.

Measurements. Explanation of the experimental equipment for conductivity measurements over a temperature range and the procedure for cell calibration using dilute aqueous potassium chloride solutions have been published previously.[7] At the beginning of every measuring series the cell was filled with a weighed amount of solvent and the solvent conductivity was determined at each temperature of the program. Weighed amounts of stock solutions of NaSCN were added using a gastight syringe, and the conductivity was measured at each temperature under pure nitrogen.

The molar concentrations c at molonity $\tilde{m}$ (mole per kilogram of solution) and temperature T are given by the relationship

$$c = \tilde{m} d; \quad d(T,\tilde{m}) = d_0(T) + D\tilde{m} \tag{1}$$

The solution densities were determined with a vibration tube densimeter,[13] yielding density coefficients D of 0.043 kg^2·dm^{-3}·mol^{-1} (propan-1-ol) and 0.025 kg^2·dm^{-3}·mol^{-1} (propan-2-ol).

The temperature-dependent solvent viscosities, densities, and permittivities for propan-1-ol and the temperature-dependent densities and permittivities of propan-2-ol given in Table 1 were taken from the literature. The temperature-dependent viscosity of propan-2-ol was determined by the use of the methods of our laboratory.

The measuring data of molar conductivity as a function of molality and temperature are given in Table 2.

Data Analysis. The analysis of conductivity data in the framework of the lcCM model proceeds by means of the following set of equations:

$$\frac{\Lambda}{\alpha} = \Lambda^\infty - S\sqrt{\frac{\alpha c}{c^\circ}} + E\frac{\alpha c}{c^\circ}\ln\frac{\alpha c}{c^\circ} + J_1\frac{\alpha c}{c^\circ} + J_2\left(\frac{\alpha c}{c^\circ}\right)^{3/2} \tag{2}$$

$$K_A = \frac{1-\alpha}{\alpha^2 c y_\pm'^2}; \quad y_\pm' = \exp\left(-\frac{\kappa q}{1+\kappa R}\right); \quad c^\circ = 1\ \text{mol·dm}^{-3} \tag{3}$$

where Λ and Λ^∞ are the molar conductivities at molarity c and infinite dilution, $(1 - \alpha)$ is the fraction of oppositely charged ions acting as ion pairs, and K_A is the equilibrium constant in terms of ion and ion-pair concentrations. $y_\pm'$ is the mean activity coefficient for the dissociated part of the electrolyte (the so-called "free" ions). The Debye parameter κ is given by

$$\kappa^2 = 16\pi N_A q\alpha c; \quad q = \frac{e^2}{8\pi\epsilon_0\epsilon kT} \tag{4}$$

e is the proton charge, ϵ is the relative permittivity of the

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Table 1. Solvent Properties of Propan-1-ol and Propan-2-ol

	$T = 228.15$ K	$T = 238.15$ K	$T = 248.15$ K	$T = 258.15$ K	$T = 268.15$ K	$T = 278.15$ K	$T = 288.15$ K	$T = 298.15$ K
				Propan-1-ol				
d^a/kg·dm^{-3}	0.8549	0.8470	0.8391	0.8312	0.8233	0.8154	0.8075	0.7996
ϵ	32.26	30.23	28.33	26.54	24.87	23.30	21.84	20.46
$10^3\eta^a$/Pa·s	16.503	11.291	7.956	5.759	4.272	3.239	2.503	1.967
				Propan-2-ol				
d^b/kg·dm^{-3}	0.8404	0.8325	0.8245	0.8163	0.8079	0.7994	0.7908	0.7819
ϵ^b	32.25	29.81	27.55	25.46	23.53	21.75	20.10	18.57
$10^3\eta^c$/Pa·s	(28.9)	(18.2)	11.917	7.984	5.436	3.866	2.881	2.104

[a] Data from ref 4. [b] Interpolated from refs 8−12. [c] Values at 228.15 K and 238.15 K estimated from the temperature-independent Walden product.

Table 2. Molar Conductivities of NaSCN Solutions[a]

	$10^4\Lambda$/S·m^2·mol^{-1}							
$10^4\tilde{m}$/mol·kg^{-1}	$T = 228.15$ K	$T = 238.15$ K	$T = 248.15$ K	$T = 258.15$ K	$T = 268.15$ K	$T = 278.15$ K	$T = 288.15$ K	$T = 298.15$ K
				Propan-1-ol				
2.823	2.730	3.974	5.597	7.677	10.295	13.593	17.543	22.254
6.401	2.648	3.849	5.411	7.404	9.888	12.944	16.635	20.991
9.407	2.595	3.767	5.291	7.225	9.639	12.588	16.123	20.266
12.018	2.555	3.708	5.198	7.093	9.446	12.318	15.741	19.737
15.100	2.515	3.646	5.107	6.960	9.256	12.044	15.358	19.204
18.353	2.478	3.587	5.023	6.837	9.079	11.795	15.011	18.724
21.373	2.447	3.541	4.953	6.735	8.930	11.588	14.726	18.333
25.591	2.407	3.482	4.866	6.608	8.755	11.335	14.376	17.852
29.691	2.374	3.432	4.791	6.499	8.599	11.120	14.075	17.442
33.449	2.345	3.388	4.727	6.408	8.468	10.938	13.827	17.110
				Propan-2-ol				
3.790	1.454	2.295	3.489	5.130	7.323	10.167	13.719	17.994
8.616	1.378	2.166	3.270	4.771	6.749	9.257	12.322	15.868
11.901	1.337	2.094	3.153	4.585	6.454	8.807	11.649	14.890
16.163	1.297	2.025	3.040	4.403	6.173	8.380	11.013	13.976
21.127	1.256	1.958	2.928	4.228	5.902	7.975	10.423	13.143
24.380	1.234	1.919	2.866	4.130	5.753	7.752	10.102	12.697
29.091	1.203	1.869	2.785	4.004	5.560	7.471	9.700	12.145
33.052	1.181	1.831	2.726	3.912	5.423	7.268	9.414	11.754
38.530	1.154	1.786	2.653	3.800	5.255	7.023	9.068	11.287
42.740	1.135	1.754	2.604	3.722	5.139	6.857	8.838	10.975

[a] The dimensions of the molonity $\tilde{m}$ are mole per kilogram of solution.

solvent, and ϵ_0 is the permittivity of the vacuum. The other coefficients have their usual meaning.

The coefficients of eq 2 are given in the literature.[14] The limiting slope S and the parameter E are completely calculable when the solvent data are available. The coefficients J_1 and J_2 are functions of the distance parameter R, representing the distance to which oppositely charged ions can approach as freely moving particles in the solution and therefore, on the other hand, the upper limit of ion association to ion pairs represented by the distance parameter R of the mean activity coefficient $y'_{\pm}$, eq 3, where $R = a + s$ ($a = a_+ + a_-$ is the sum of the ionic radii of cation and anion, and s is the length of orientated solvent molecules in the ion pair).

The advantageously used three-parameter fits for conductivity, setting the coefficients S, E, and J_1 of eq 2 to their theoretical values, yield the limiting values of the molar conductivity Λ^∞, the association constant K_A, and the coefficient J_2 by nonlinear least squares iterations.

Figures 1 (propan-1-ol solutions) and 2 (propan-2-ol solutions) show the temperature dependence of the molar conductivity. Comparison is made with literature values at 25 °C.

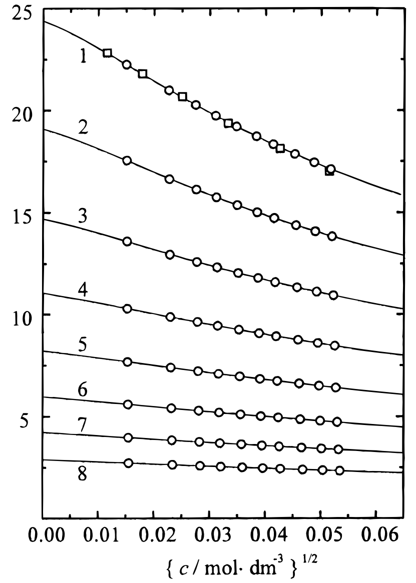

Figure 1. Molar conductivity of NaSCN in propan-1-ol: ○, this paper; □, ref 2; 1, 25 °C; 2, 15 °C; 3, 5 °C; 4, −5 °C; 5, −15 °C; 6, −25 °C; 7, −35 °C; 8, −45 °C.

Results and Discussion

Table 3 gives the values of Λ^∞, J_2, and K_A obtained by the use of three-parameter fits with $R = a + s$. The choice of a temperature-independent distance parameter $R = a + s = 1.405$ nm (propan-1-ol) and 1.345 nm (propan-2-ol), taking into account solvent-separated ion pairs, is justified by a multitude of data analyses on alcohol solutions of lithium and sodium salts collected in the DECHEMA

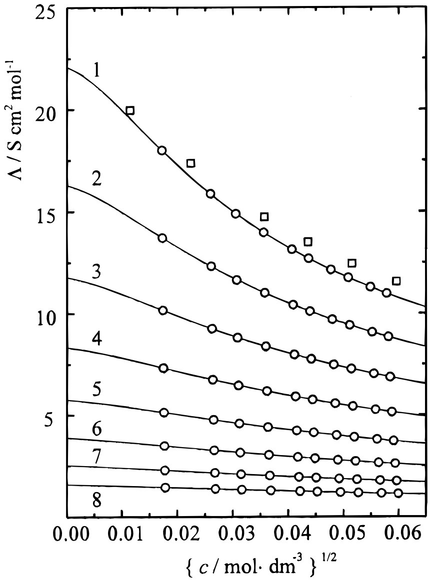

Figure 2. Molar conductivity of NaSCN in propan-2-ol: ○, this paper; □, ref 3; 1, 25 °C; 2, 15 °C; 3, 5 °C; 4, −5 °C; 5, −15 °C; 6, −25 °C; 7, −35 °C; 8, −45 °C.

Table 3. Limiting Conductivities and Association Constants of NaSCN Solutions

T / K	$10^4\Lambda^\infty$ / $S \cdot m^2 \cdot mol^{-1}$	K_A / $dm^3 \cdot mol^{-1}$	$10^4 J_2$ / $S \cdot m^2 \cdot mol^{-1}$	$10^{-4}\sigma$ / $S \cdot m^2 \cdot mol^{-1}$
		Propan-1-ol		
228.15	2.897	66.86	994.5	0.001
238.15	4.226	75.21	1519.6	0.002
248.15	5.970	86.19	2246.3	0.003
258.15	8.215	99.34	3318.3	0.004
268.15	11.057	118.16	4673.1	0.005
278.15	14.690	159.54	5326.1	0.009
288.15	19.079	192.82	7500.6	0.009
298.15	24.388	235.42	10766.8	0.009
		Propan-2-ol		
228.15	1.592	139.12	414.0	0.001
238.15	2.527	171.41	751.1	0.001
248.15	3.873	212.27	1221.1	0.002
258.15	5.756	259.65	2040.9	0.003
268.15	8.336	326.30	3302.3	0.004
278.15	11.783	422.71	5198.4	0.005
288.15	16.276	561.84	8246.6	0.007
298.15	22.075	777.82	12249.7	0.008

[a] Standard deviation $\sigma^2 = \sum(\Lambda_{exp} - \Lambda_{calc})^2/3$.

Chemistry Data Series, Vol. XII, parts 1 (methanol), 1a (ethanol), and 1b (propanol and higher alcohols).

The coefficient $J_2(R)$ of eq 2 has no proper significance for the discussion of electrolyte solution structures and is not considered in the following discussion. It has importance only as a parameter for a complete reproduction of the conductivity data, which is given by the full lines in Figures 1 and 2.

Expectedly, the molar conductivities at infinite dilution of propan-1-ol are larger than those of propan-2-ol, in agreement with the solvent viscosities. Molar conductivities Λ^∞ mainly reflect the electrophoretic effect on conductivity. The temperature dependence of Λ^∞ (Figure 3) may be represented in the framework of the kinetic conductance theory[15] by the equation

$$\ln \Lambda^\infty + \frac{2}{3}\ln d = \frac{\Delta H^\ddagger}{RT} + B \qquad (5)$$

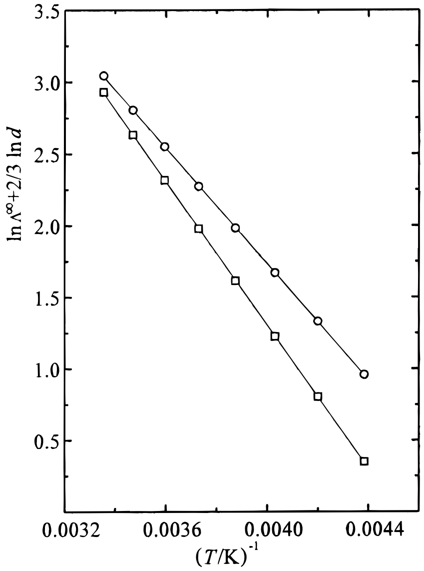

Figure 3. Determination of the activation energy of the transport process according to eq 5: ○, NaSCN in propan-1-ol; □, NaSCN in propan-2-ol.

where d is the density of the solvent and $\Delta H^\ddagger$ is the activation energy of the transport process. From the linear functions of Figure 3 we obtain $\Delta H^\ddagger = 17$ kJ mol^{-1} (propan-1-ol) and 21 kJ mol^{-1} (propan-2-ol). In comparison, 18 kJ mol^{-1} was found for Pr_4NBr and Pr_4NI in propan-1-ol.[16] The temperature dependence of the Walden product $\Lambda^\infty\eta$ (Table 4) is very small as always found for alkali metal salts in ethanol and propanol solutions, except for lithium salts, which show a negative slope of $\Lambda^\infty\eta$.

Also, the association constants K_A of NaSCN in the two solvents show the expected behavior. Ion-pair formation in propan-1-ol is smaller than that in propan-2-ol at every temperature due to the higher permittivity of propan-1-ol. The representation of ln K_A versus reciprocal temperature is nonlinear in both solvents and can be satisfactorily represented by a polynomial of second degree. The Gibbs energy of ion-pair formation $\Delta G°_A$ is negative in both solvents at all temperatures, and the enthalpy and entropy of the association process according to

$$\Delta G°_A = -RT \ln K_A; \quad \Delta S°_A = -\left(\frac{\partial \Delta G°_A}{\partial T}\right)_p;$$
$$\Delta H°_A = -T^2\left(\frac{\partial \Delta G°_A/T}{\partial T}\right)_p \qquad (6)$$

yield positive temperature-dependent values of $\Delta H°_A$ and $\Delta S°_A$; see Figure 4.

The separation of the electrostatic (superscript: el) and nonelectrostatic effects (superscript: *) is possible in the thermodynamic functions $\Delta G°_A$, $\Delta S°_A$, and $\Delta H°_A$ by setting $\Delta G°_A = \Delta G^{el}_A + \Delta G^*_A$ and so forth.

For this purpose the association constant of the lcCM is used[4]

$$K_A = 4\pi N_A \int_a^R r^2 \exp\left[\frac{2q}{r} - \frac{W^*(r)}{kT}\right] dr \qquad (7)$$

where $W^*(r)$ is the mean force potential of the nonelectrostatic forces in the region $a \le r \le R$, which commonly is introduced as a temperature-dependent step potential:

$$W^*(r) = \text{const} \quad \text{for} \quad a \le r \le R$$
$$W^*(r) = 0 \quad \text{for} \quad R \le r \le \infty \qquad (8)$$

Table 4. Walden Product

	$T = 228.15$ K	$T = 238.15$ K	$T = 248.15$ K	$T = 258.15$ K	$T = 268.15$ K	$T = 278.15$ K	$T = 288.15$ K	$T = 298.15$ K
				Propan-1-ol				
$10^7\Lambda^\infty\eta$/S·m^2·mol^{-1}·Pa·s	47.81	47.72	47.50	47.31	47.24	47.58	47.75	47.97
				Propan-2-ol				
$10^7\Lambda^\infty\eta$/S·m^2·mol^{-1}·Pa·s	(46.0)	(46.0)	46.15	45.96	45.31	45.55	46.89	46.45

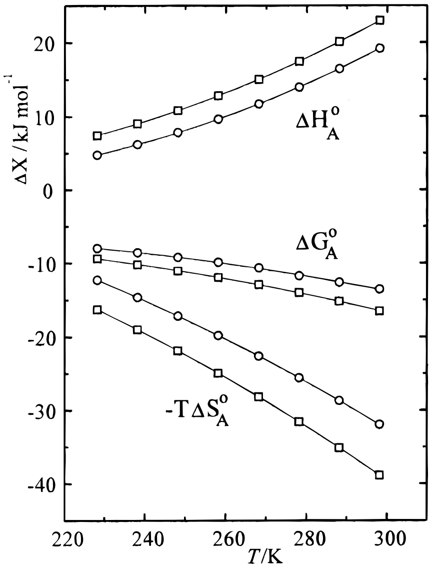

Figure 4. Thermodynamic functions for ion-pair formation. ΔX is the Gibbs energy, enthalpy, and entropy: ○, NaSCN in propan-1-ol; □, NaSCN in propan-2-ol.

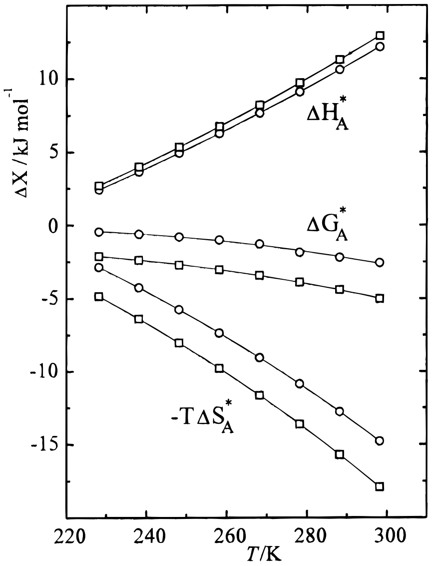

Figure 5. Nonelectrostatic parts ΔX of the Gibbs energy G, enthalpy H, and entropy S of ion-pair formation: ○, NaSCN in propan-1-ol; □, NaSCN in propan-2-ol.

Then by definition it follows that $\Delta G°_A = N_A W^*(r)$ and

$$K_A = 4\pi N_A \exp\left[-\frac{\Delta G^*_A}{RT}\right]\int_a^R r^2 \exp\left(\frac{2q}{r}\right) \mathrm{d}r \qquad (9)$$

Knowing K_A and R from the conductivity measurements as a function of temperature, the quantities ΔS^*_A and ΔH^*_A are available from equations corresponding to eq 6. Figure 5 shows that also $\Delta G^*_A < 0$, $\Delta S^*_A > 0$, and $\Delta H^*_A > 0$, reflecting a behavior comparable with the results known from temperature-dependent conductivity measurements on simple alkali metal salts in alcohol solutions which are discussed in comparison with other types of salts of different behavior in earlier papers.[4,17]

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