

Studies on Molecular Interactions of Some Thiocyanate Salts in Coaqueous Solutions of 1,3-Dioxolane + Water by Volumetric, Viscometric, and Speed of Sound Measurements

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The densities and viscosities of some thiocyanate compounds, viz., ammonium thiocyanate, sodium thiocyanate, and potassium thiocyanate, in 10 %, 20 %, and 30 % by mass of 1,3-dioxolane + water mixtures have been determined at $T = (298.15, 308.15, \text{ and } 318.15) \text{ K}$ and $p = 0.1 \text{ MPa}$. The speeds of sound of the thiocyanate compounds in 10 %, 20 %, and 30 % by mass of 1,3-dioxolane + water mixtures have also been determined at 298.15 K. Apparent molar volumes (V_ϕ), viscosity B -coefficients, and adiabatic compressibility (β) of these electrolytes were obtained from their densities, viscosities, and speed of sound data. The limiting apparent molar volumes (V_ϕ°) and experimental slopes (S_v^*) derived from the Masson equation and the obtained parameters have been interpreted in terms of ion–solvent and ion–ion interactions, respectively. The viscosity data were evaluated by using the Jones–Dole equation. The structure making/breaking capacities of the electrolytes have been inferred from the sign of $(\delta^2\phi_v^\circ/\delta T^2)_p$ and dB/dT . The activation parameters of viscous flow for the ternary solutions studied were also calculated and explained by the application of transition state theory.

Introduction

It is well-known that the reaction medium plays an important role in determining reactivity reflected in thermodynamic, transport, and spectral properties.^{1,2} Gaining insight into the mechanism of such interactions, thermodynamic and transport studies involving one or more solutes in mixed solvent systems are highly useful. Studies on the apparent molar volumes of electrolytes and the dependence of viscosity in connection with solutes and temperature of solutions have been employed as a function of studying ion–ion and ion–solvent interactions.³ The finding of a number of workers^{4–7} is that the addition of electrolyte could break or make the structure of a liquid. The addition of organic solvent to an aqueous solution of electrolyte brings about a change in the ion's solvation and often results in a large change in the reactivity of the dissolved electrolytes. The viscosity being a property of the liquid depending on intermolecular forces, the structural aspects of the liquid can be inferred from the viscosity of solutions at different concentrations and temperatures.

1,3-Dioxolane is a good industrial solvent. It figures prominently in the high energy battery industry and finds application in organic synthesis as manifested from the physicochemical studies in this medium.⁸ In the present study, we have performed density, viscosity, and speed of sound measurements in 10 %, 20 %, and 30 % by mass of 1,3-dioxolane + water mixtures of ammonium thiocyanate, sodium thiocyanate, and potassium thiocyanate as a function of temperature to unravel the nature of various types of interactions prevailing in these electrolyte solutions.

Experimental Section

Materials. 1,3-Dioxolane, $\text{C}_3\text{H}_6\text{O}_2$ (ethylene glycol formal or ethylene glycol methylene ether) from Merck, containing 0.3 %

Table 1. Physical Properties of Pure 1,3-Dioxolane and 1,3-Dioxolane + Water Mixtures at Different Temperatures

temperature	$\rho \cdot 10^{-3} / \text{kg} \cdot \text{m}^{-3}$		$\eta / \text{mPa} \cdot \text{s}$	
	observed	literature	observed	literature
10 % by mass of 1,3-dioxolane + water				
298.15 K	1013.40	---	0.9970	---
308.15 K	1007.40	---	0.8350	---
318.15 K	1003.90	---	0.7452	---
20 % by mass of 1,3-dioxolane + water				
298.15 K	1024.70	---	1.1240	---
308.15 K	1018.70	---	0.9652	---
318.15 K	1013.80	---	0.8548	---
30 % by mass of 1,3-dioxolane + water				
298.15 K	1034.20	---	1.2460	---
308.15 K	1027.80	---	1.0618	---
318.15 K	1021.30	---	0.9373	---
pure 1,3-dioxolane				
298.15 K	1058.6	1058.62 ¹⁴	0.5886	0.5889 ¹⁴
308.15 K	1045.8	---	0.5235	---
318.15 K	1035.6	---	0.4584	---

water and 0.005 % peroxides and sterilized with butylated hydroxytoluene (BHT) was purified by heating under reflux with PbO_2 for 2 h, then cooled and filtered. After adding xylene to the filtrate, the mixture was fractionally distilled.^{9,10} The solvent obtained after purification had a boiling point of 348 K at $p = 0.1 \text{ MPa}$, a density of $1058.6 \text{ kg} \cdot \text{m}^{-3}$, and a coefficient of viscosity of $0.5750 \text{ mPa} \cdot \text{s}$ at 298.15 K which is in good agreement with literature values.^{10,11} The purity of the solvent finally obtained was > 99.0 %.

Ammonium thiocyanate, sodium thiocyanate, and potassium thiocyanate (NH_4CNS , NaCNS , and KCNS) salts (all A.R., B.D.H.) were purified by recrystallization twice from triply distilled water with a specific conductance of less than $10^{-6} \text{ S} \cdot \text{cm}^{-1}$ at 298.15 K. The samples were dried in vacuum and stored over P_2O_5 under vacuum.

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Table 2. Concentration c , Density ρ , Viscosity η , Apparent Molar Volumes V_ϕ , and $(\eta_r - 1)/c^{1/2}$ for Ammonium Thiocyanate, Sodium Thiocyanate, and Potassium Thiocyanate in Different Coaqueous (1,3-Dioxolane + Water) Solutions at Different Temperatures

c mol·dm ⁻³	$\rho \cdot 10^{-3}$ kg·m ⁻³	η mPa·s	$V_\phi \cdot 10^6$ m ³ ·mol ⁻¹	$(\eta_r - 1)/c^{1/2}$	c mol·dm ⁻³	$\rho \cdot 10^{-3}$ kg·m ⁻³	η mPa·s	$V_\phi \cdot 10^6$ m ³ ·mol ⁻¹	$(\eta_r - 1)/c^{1/2}$
Ammonium Thiocyanate									
10 % by Mass of 1,3-Dioxolane + Water									
$T = 298.15$ K									
0.00198	1013.50	1.0046	26.000	0.1720	0.03767	1015.57	1.0438	18.401	0.2420
0.01388	1014.14	1.0212	22.799	0.2060	0.04957	1016.30	1.0540	17.300	0.2570
0.02578	1014.83	1.0333	20.402	0.2270	0.06147	1017.05	1.0630	16.501	0.2670
$T = 308.15$ K									
0.00197	1007.48	0.8399	37.399	0.1330	0.03742	1009.20	0.8699	27.784	0.2160
0.01379	1007.99	0.8522	32.995	0.1750	0.04923	1009.82	0.8782	26.677	0.2330
0.02561	1008.57	0.8613	30.290	0.1970	0.06104	1010.52	0.8855	24.772	0.2450
$T = 318.15$ K									
0.00196	1003.95	0.7485	51.500	0.1003	0.03728	1005.22	0.7727	40.496	0.1910
0.01374	1004.31	0.7580	46.199	0.1460	0.04903	1005.74	0.7795	38.494	0.2080
0.02551	1004.74	0.7654	43.197	0.1700	0.06078	1006.33	0.7867	35.993	0.2260
20 % by Mass of 1,3-Dioxolane + Water									
$T = 298.15$ K									
0.00199	1024.80	1.1343	24.800	0.2060	0.03775	1026.87	1.1821	18.100	0.2660
0.01391	1025.45	1.1551	21.600	0.2350	0.04967	1027.61	1.1939	17.200	0.2790
0.02583	1026.15	1.1692	19.500	0.2500	0.06158	1028.39	1.2038	15.800	0.2860
$T = 308.15$ K									
0.00198	1018.78	0.9721	32.799	0.1600	0.03750	1020.59	1.0089	25.183	0.2340
0.01382	1019.34	0.9876	28.995	0.1970	0.04933	1021.28	1.0179	23.378	0.2460
0.02566	1019.95	0.9989	26.989	0.2180	0.06116	1021.97	1.0277	22.172	0.2620
$T = 318.15$ K									
0.00197	1013.86	0.8591	44.678	0.1130	0.03731	1015.33	0.8886	34.529	0.2050
0.01375	1014.29	0.8708	39.609	0.1600	0.04907	1015.93	0.8965	32.291	0.2200
0.02553	1014.80	0.8801	36.563	0.1850	0.06084	1016.55	0.9041	30.459	0.2340
30 % by Mass of 1,3-Dioxolane + Water									
$T = 298.15$ K									
0.00206	1034.31	1.2578	23.700	0.2090	0.03809	1036.38	1.3100	18.200	0.2630
0.01406	1034.96	1.2809	21.501	0.2360	0.04980	1037.07	1.3225	17.800	0.2750
0.02636	1035.68	1.2968	19.401	0.2510	0.06205	1037.86	1.3341	16.502	0.2840
$T = 308.15$ K									
0.00205	1027.90	1.0697	28.700	0.1650	0.03783	1029.82	1.1089	21.990	0.2280
0.01397	1028.49	1.0862	25.797	0.1942	0.04945	1030.50	1.1180	20.985	0.2380
0.02619	1029.16	1.0982	23.493	0.2120	0.06161	1031.24	1.1269	19.781	0.2470
$T = 318.15$ K									
0.00204	1021.37	0.9428	41.004	0.1290	0.03758	1022.93	0.9718	32.188	0.1900
0.01388	1021.84	0.9545	36.515	0.1560	0.04912	1023.50	0.9799	30.589	0.2050
0.02602	1022.38	0.9636	34.010	0.1740	0.06119	1024.17	0.9881	28.669	0.2190
Sodium Thiocyanate									
10 % by Mass of 1,3-Dioxolane + Water									
$T = 298.15$ K									
0.00199	1013.50	1.0047	28.001	0.1730	0.03773	1015.69	1.0446	20.000	0.2460
0.01390	1014.19	1.0216	24.000	0.2090	0.04964	1016.49	1.0554	18.599	0.2630
0.02581	1014.92	1.0343	21.800	0.2330	0.06156	1017.31	1.0655	17.300	0.2770
$T = 308.15$ K									
0.00197	1007.47	0.8400	43.300	0.1350	0.03749	1009.25	0.8711	31.398	0.2230
0.01381	1008.00	0.8523	37.600	0.1760	0.04932	1009.91	0.8799	29.998	0.2420
0.02565	1008.61	0.8619	33.700	0.2010	0.06115	1010.64	0.8879	27.803	0.2560
$T = 318.15$ K									
0.00197	1003.95	0.7487	56.800	0.1050	0.03734	1005.29	0.7740	43.802	0.2000
0.01376	1004.31	0.7577	50.901	0.1430	0.04912	1005.85	0.7814	41.305	0.2190
0.02556	1004.78	0.7659	46.501	0.1740	0.06090	1006.46	0.7884	38.808	0.2350
20 % by Mass of 1,3-Dioxolane + Water									
$T = 298.15$ K									
0.00201	1024.81	1.1344	26.900	0.2055	0.03825	1027.03	1.1835	19.700	0.2706
0.01409	1025.50	1.1558	23.500	0.2380	0.05033	1027.85	1.1956	18.000	0.2840
0.02617	1026.26	1.1708	21.100	0.2572	0.06240	1028.67	1.2066	17.100	0.2940
$T = 308.15$ K									
0.00200	1018.78	0.9722	39.200	0.1617	0.03800	1020.68	1.0105	28.502	0.2407
0.01401	1019.35	0.9877	33.901	0.1970	0.05000	1021.39	1.0207	26.704	0.2572
0.02601	1019.99	0.9998	30.703	0.2220	0.06199	1022.16	1.0300	24.806	0.2695

Table 2 Continued

c mol·dm ⁻³	$\rho \cdot 10^{-3}$ kg·m ⁻³	η mPa·s	$V_\phi \cdot 10^6$ m ³ ·mol ⁻¹	$(\eta_r - 1)/c^{1/2}$	c mol·dm ⁻³	$\rho \cdot 10^{-3}$ kg·m ⁻³	η mPa·s	$V_\phi \cdot 10^6$ m ³ ·mol ⁻¹	$(\eta_r - 1)/c^{1/2}$
<i>T</i> = 318.15 K									
0.00199	1013.86	0.8592	49.100	0.1152	0.03781	1015.44	0.8900	37.105	0.2119
0.01394	1014.35	0.8709	40.803	0.1600	0.04974	1016.08	0.8994	34.707	0.2340
0.02588	1014.86	0.8806	39.703	0.1880	0.06167	1016.73	0.9076	33.108	0.2490
30 % by Mass of 1,3-Dioxolane + Water									
<i>T</i> = 298.15 K									
0.00215	1034.32	1.2579	24.899	0.2060	0.04051	1036.72	1.3125	18.201	0.2650
0.01497	1035.09	1.2818	21.200	0.2350	0.05182	1037.47	1.3246	17.300	0.2770
0.02780	1035.89	1.2984	19.499	0.2520	0.06662	1038.50	1.3383	16.000	0.2870
<i>T</i> = 308.15 K									
0.00213	1027.91	1.0699	30.302	0.1650	0.04024	1030.16	1.1112	21.800	0.2320
0.01487	1028.60	1.0869	26.396	0.1940	0.05148	1030.90	1.1206	20.249	0.2440
0.02762	1029.37	1.1003	23.576	0.2180	0.06617	1031.89	1.1328	18.711	0.2600
<i>T</i> = 318.15 K									
0.00212	1021.38	0.9429	44.001	0.1290	0.03997	1023.15	0.9753	33.962	0.2030
0.01478	1021.90	0.9553	39.401	0.1580	0.05112	1023.75	0.9833	32.459	0.2170
0.02744	1022.50	0.9652	36.381	0.1800	0.06570	1024.58	0.9926	30.427	0.2300
Potassium Thiocyanate									
10 % by Mass of 1,3-Dioxolane + Water									
<i>T</i> = 298.15 K									
0.00199	1013.53	1.0048	33.001	0.1750	0.03776	1016.19	1.0528	23.000	0.2880
0.01391	1014.37	1.0242	26.900	0.2310	0.04968	1017.15	1.0659	21.501	0.3100
0.02583	1015.25	1.0393	25.101	0.2640	0.06160	1018.18	1.0782	19.400	0.3280
<i>T</i> = 308.15 K									
0.00197	1007.50	0.8401	48.490	0.1380	0.03752	1009.69	0.8758	35.999	0.2520
0.01382	1008.17	0.8540	41.500	0.1940	0.04939	1010.53	0.8866	33.499	0.2780
0.02566	1008.89	0.8652	38.799	0.2260	0.06127	1011.40	0.8958	31.699	0.2940
<i>T</i> = 318.15 K									
0.00197	1003.96	0.7487	64.294	0.1060	0.03737	1005.69	0.7772	49.199	0.2220
0.01377	1004.46	0.7591	56.400	0.1590	0.04919	1006.39	0.7855	46.299	0.2440
0.02556	1005.04	0.7680	52.399	0.1910	0.06101	1007.15	0.7949	43.798	0.2700
20 % by Mass of 1,3-Dioxolane + Water									
<i>T</i> = 298.15 K									
0.00209	1024.84	1.1345	30.333	0.2039	0.03977	1027.67	1.1863	21.999	0.2780
0.01465	1025.73	1.1562	26.022	0.2370	0.05234	1028.69	1.1988	20.466	0.2910
0.02721	1026.68	1.1722	23.723	0.2600	0.06490	1029.75	1.2113	18.933	0.3050
<i>T</i> = 308.15 K									
0.00208	1018.81	0.9724	44.625	0.1630	0.03952	1021.20	1.0111	33.396	0.2390
0.01457	1019.54	0.9880	38.939	0.1960	0.05200	1022.10	1.0222	31.203	0.2590
0.02705	1020.34	1.0001	35.910	0.2200	0.06447	1023.03	1.0328	29.449	0.2760
<i>T</i> = 318.15 K									
0.00207	1013.88	0.8593	55.461	0.1160	0.03932	1015.96	0.8909	41.560	0.2130
0.01449	1014.49	0.8712	49.128	0.1590	0.05173	1016.79	0.9008	38.887	0.2364
0.02691	1015.19	0.8810	44.749	0.1870	0.06413	1017.66	0.9098	36.560	0.2540
30 % by Mass of 1,3-Dioxolane + Water									
<i>T</i> = 298.15 K									
0.00215	1034.35	1.2581	28.485	0.2100	0.04051	1037.28	1.3160	20.408	0.2790
0.01497	1035.27	1.2818	24.582	0.2350	0.05182	1038.30	1.3288	17.515	0.2920
0.02780	1036.29	1.2996	21.375	0.2580	0.06662	1039.41	1.3444	18.311	0.3060
<i>T</i> = 308.15 K									
0.00213	1027.92	1.0700	39.958	0.1680	0.04024	1030.48	1.1125	29.799	0.2380
0.01487	1028.71	1.0874	34.883	0.1980	0.05148	1031.42	1.1227	26.222	0.2530
0.02762	1029.59	1.1006	31.452	0.2200	0.06617	1032.43	1.1358	26.409	0.2710
<i>T</i> = 318.15 K									
0.00212	1021.40	0.9430	50.382	0.1320	0.03997	1023.65	0.9791	37.556	0.2230
0.01478	1022.07	0.9568	44.032	0.1710	0.05113	1024.50	0.9877	33.948	0.2380
0.02744	1022.86	0.9676	39.553	0.1950	0.06572	1025.44	0.9993	33.479	0.2580

Table 3. Limiting Partial Molar Volume V_{ϕ}° and Experimental Slope S_v^* for Ammonium Thiocyanate, Sodium Thiocyanate, and Potassium Thiocyanate in Different Coaqueous (1,3-Dioxolane + Water) Solutions at Different Temperatures

mass fraction of 1,3-dioxolane	$V_{\phi}^{\circ} \cdot 10^6 / \text{m}^3 \cdot \text{mol}^{-1}$			$S_v^* \cdot 10^4 / \text{m}^2 \cdot \text{L}^{1/2} \cdot \text{mol}^{-3/2}$		
	$T = 298.15 \text{ K}$	$T = 308.15 \text{ K}$	$T = 318.15 \text{ K}$	$T = 298.15 \text{ K}$	$T = 308.15 \text{ K}$	$T = 318.15 \text{ K}$
	Ammonium Thiocyanate					
10	28.216	40.184	55.024	-48.497	-62.078	-75.578
20	26.708	35.211	47.804	-43.754	-52.505	-69.906
30	25.382	30.792	43.685	-35.408	-44.380	-59.913
	Sodium Thiocyanate					
10	30.267	46.455	60.951	-52.520	-76.063	-89.101
20	29.120	42.232	51.500	-48.659	-70.161	-75.294
30	26.557	32.948	47.102	-41.319	-55.592	-64.970
	Potassium Thiocyanate					
10	35.346	51.774	68.521	-63.900	-81.835	-100.370
20	32.697	47.865	59.833	-53.911	-72.830	-91.831
30	30.658	43.029	54.054	-49.746	-68.155	-84.055

Table 4. Values of Various Coefficients of Equation 4 for Different Thiocyanates in Different Coaqueous (1,3-Dioxolane + Water) Solutions

mass fraction of 1,3-dioxolane	$a_0 \cdot 10^6$			$a_1 \cdot 10^6$			$a_2 \cdot 10^6$		
	$\text{m}^3 \cdot \text{mol}^{-1}$			$\text{m}^3 \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$			$\text{m}^3 \cdot \text{mol}^{-1} \cdot \text{K}^{-2}$		
	Ammonium Thiocyanate								
10	-1329.000	7.705	-0.010						
20	803.020	-6.355	0.013						
30	27.389	-0.584	0.002						
	Sodium Thiocyanate								
10	-2623.200	16.056	-0.024						
20	1278.900	-9.638	0.019						
30	-570.480	3.120	-0.004						
	Potassium Thiocyanate								
10	220.740	-1.743	0.004						
20	3797.400	-25.738	0.044						
30	4690.500	-31.185	0.052						

Table 5. Limiting Partial Molar Expansibility ϕ_E° for Ammonium Thiocyanate, Sodium Thiocyanate, and Potassium Thiocyanate in Different Coaqueous (1,3-Dioxolane + Water) Solutions at Different Temperatures

mass fraction of 1,3-dioxolane	$\phi_E^{\circ} \cdot 10^6 / \text{m}^3 \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$			$(\delta\phi_E^{\circ} / \delta T)_p \cdot 10^6$		
	298.15 K	308.15 K	318.15 K	$\text{m}^3 \cdot \text{mol}^{-1} \cdot \text{K}^{-2}$		
	Ammonium Thiocyanate					
10	1.623	1.419	1.215	-0.020		
20	1.278	1.534	1.790	0.026		
30	0.668	0.710	0.752	0.004		
	Sodium Thiocyanate					
10	1.983	1.511	1.039	-0.047		
20	1.393	1.763	2.133	0.037		
30	0.974	0.902	0.830	-0.007		
	Potassium Thiocyanate					
10	0.881	0.969	1.057	0.009		
20	0.618	1.502	2.386	0.088		
30	0.001	1.047	2.093	0.105		

Apparatus and Procedure. The binary aqueous solution of 1,3-dioxolane as well as the solutions of thiocyanate were made by weight, and conversion of molality into molarity was done¹² using density values. Adequate precautions were made to reduce evaporation losses during mixing.

The densities (ρ) were measured with an Ostwald-Sprengel type pycnometer having a bulb volume of 25 cm³ and an internal diameter of the capillary of about 0.1 cm. The pycnometer was calibrated at the experimental temperatures with double-distilled water and benzene. The pycnometer with the test solution was equilibrated in a water-bath maintained at ± 0.01 K of the desired temperature by means of a mercury-in-glass thermoregulator, and the temperature was determined by a calibrated thermometer and

Muller bridge. The pycnometer was then removed from the thermostatic bath, properly dried, and weighed. The evaporation losses remained insignificant during the time of the actual measurements. An average of three measurements was taken into account. The density values are reproducible to $\pm 3 \cdot 10^{-4} \text{ g} \cdot \text{cm}^{-3}$. The viscosity (η) was measured by means of a suspended-level Ubbelohde¹³ viscometer at the desired temperature (precision ± 0.01 K). The uncertainty in viscosity measurements was $\pm 0.003 \text{ mPa} \cdot \text{s}$. Details have been described earlier.⁸ Speeds of sound (u) were determined with an uncertainty of $\pm 0.2 \text{ m} \cdot \text{s}^{-1}$, using a single-crystal variable-path ultrasonic interferometer (Mittal Enterprises, New Delhi, India) working at 2 MHz, which was calibrated with purified water and methanol at 298.15 K. The temperature stability was maintained within ± 0.01 K by circulating thermostatted water around the cell by a circulating pump.

Results and Discussion

The experimental values of densities and viscosities of pure¹⁴ 1,3-DO and 10 %, 20 %, and 30 % by mass of 1,3-DO + H₂O mixtures at $T = (298.15, 308.15, \text{ and } 318.15) \text{ K}$ and $p = 0.1 \text{ MPa}$ are reported in Table 1.

In the present investigation, we have determined the ρ , η , and u values, and the values of different parameters such as V_{ϕ} , V_{ϕ}° , S_v^* , A , B , ϕ_k , ϕ_k° , and S_k^* have been measured at different temperatures using the appropriate equations and graphical diagrams.

The apparent molar volumes V_{ϕ} of solutions were calculated from the density data using the following standard expression

$$V_{\phi} = M/\rho_0 - 1000(\rho - \rho_0)/c\rho_0 \quad (1)$$

where c is the molar concentration of the solution; M is the molecular weight of the solute; and the other symbols have their usual meaning.

The values of limiting apparent molar volumes V_{ϕ}° and experimental slopes S_v^* at different temperatures have been obtained by using least-squares from linear plots of V_{ϕ} against $c^{1/2}$ using the Masson equation¹⁵

$$V_{\phi} = V_{\phi}^{\circ} + S_v^* c^{1/2} \quad (2)$$

where S_v^* is a constant dependent on charge and salt type and can be related to ion-ion interactions and V_{ϕ}° is the limiting apparent molar volume which is related to ion-solvent interactions. The V_{ϕ}° values along with the experimental slopes S_v^* are listed in Table 3.

Table 6. Values of *A*- and *B*-Coefficients for Ammonium Thiocyanate, Sodium Thiocyanate, and Potassium Thiocyanate in Different Coaqueous (1,3-Dioxolane + Water) Solutions at Different Temperatures

mass fraction of 1,3-dioxolane	$A \cdot 10^{-3}/\text{m}^{3/2} \cdot \text{mol}^{-1/2}$			$B \cdot 10^6/\text{m}^3 \cdot \text{mol}^{-1}$		
	$T = 298.15 \text{ K}$	$T = 308.15 \text{ K}$	$T = 318.15 \text{ K}$	$T = 298.15 \text{ K}$	$T = 308.15 \text{ K}$	$T = 318.15 \text{ K}$
	Ammonium Thiocyanate					
10	0.151	0.109	0.073	0.471	0.555	0.614
20	0.188	0.138	0.088	0.400	0.494	0.597
30	0.192	0.146	0.106	0.368	0.410	0.444
	Sodium Thiocyanate					
10	0.150	0.107	0.072	0.507	0.602	0.658
20	0.186	0.136	0.083	0.433	0.536	0.665
30	0.188	0.142	0.102	0.386	0.451	0.496
	Potassium Thiocyanate					
10	0.142	0.103	0.067	0.752	0.775	0.804
20	0.180	0.134	0.081	0.486	0.543	0.671
30	0.184	0.142	0.100	0.468	0.489	0.606

The plots of V_ϕ against the square root of the molar concentration $c^{1/2}$ were found to be linear with negative slopes. Table 3 shows that the limiting apparent molar volumes V_ϕ° for all studied mixtures are positive and increase with a rise in temperature but decrease with an increase in the amount of 1,3-dioxolane in the mixtures.

This indicates the presence of strong ion–solvent interactions, and these interactions are further strengthened with a rise in temperature and weakened with an increase in the amount of 1,3-dioxolane in the mixed solvent under investigation, suggesting larger electrostriction at higher temperature and lower amount of 1,3-dioxolane in the mixture. Similar results were obtained for some 1:1 electrolytes in aqueous *N,N*-dimethylformamide (DMF)¹⁶ and aqueous tetrahydrofuran (THF).¹⁷

It is evident from Table 3 that the values of S_v^* for all the studied mixtures are negative at all temperatures. Since S_v^* is a measure of ion–ion interactions, the results indicate the presence of weak ion–ion interactions. These interactions, however, decrease with a rise in temperature, which is attributed to more violent thermal agitation at higher temperature, resulting in a diminished force of ion–ion interactions (ionic dissociation).^{2,18} The S_v^* values increase with an increase in the amount of 1,3-dioxolane in the mixture which results in a decrease in the solvation of ions; i.e., more and more solute is accommodated in the void space left in the packing of large associated solvent molecules with the addition of 1,3-dioxolane to the mixture.

Since the thiocyanate ion is common in the cases of the studied salts, from the values of V_ϕ° at a particular temperature, it may be concluded that the solvation of cations in the 1,3-dioxolane + water mixture follows the order $\text{K}^+ > \text{Na}^+ > \text{NH}_4^+$. The same results are observed for some metal sulfates in water.^{2,19}

The temperature dependence of V_ϕ° for various thiocyanate salts, studied here in the solvent mixtures, can be expressed by the polynomial

$$V_\phi^\circ = a_0 + a_1T + a_2T^2 \quad (3)$$

where T is the temperature in Kelvin. The values of coefficients a_0 , a_1 , and a_2 for all the studied mixtures are reported in Table 4.

The apparent molar expansibilities ϕ_E° at infinite dilution can be obtained by differentiating eq 3 with respect to temperature

$$\phi_E^\circ = (\delta V_\phi^\circ / \delta T)_p = a_1 + 2a_2T \quad (4)$$

The values of ϕ_E° along with the sign of magnitude of $(\delta^2 V_\phi^\circ / \delta T^2)_p$ for the studied mixtures at all temperatures are reported in Table 5.

Hepler²⁰ has developed a technique of examining the sign of $(\delta^2 V_\phi^\circ / \delta T^2)_p$ for various solutes in terms of long-range structure making or breaking capacities of the solutes in mixed solvent systems using the following thermodynamic expression

$$(\delta C_p / \delta P)_T = -(\delta^2 V_\phi^\circ / \delta T^2)_p \quad (5)$$

On the basis of eq 5, it has been deduced that the structure breaker solutes should have small positive or negative values, otherwise it is a structure maker. In the present study, it is observed from Table 5 that the electrolytes (viz., NH_4SCN , NaSCN , and KSCN) under investigation are predominantly structure breakers in all the experimental solvent mixtures. This may be ascribed to the absence of caging or packing effects.^{17,21}

The viscosity data of all studied mixtures have been analyzed by the Jones–Dole²² equation

$$(\eta/\eta_o - 1)/c^{1/2} = (\eta_r - 1)/c^{1/2} = A + Bc^{1/2} \quad (6)$$

where $\eta = (Kt - Lt)\rho$; $\eta_r = \eta/\eta_o$ and η are the viscosities of solvent and solution, respectively; c is the molar concentration of a solution; ρ is the density of the solution; and K and L are constants for a particular viscometer. The values of A and B have been determined from the intercept and slope of linear plots of $(\eta/\eta_o - 1)/c^{1/2}$ versus $c^{1/2}$ and are recorded in Table 6.

It is evident from Table 6 that in all cases small positive values of A -coefficients continuously decrease with the rise in temperature but increase with an increase in the amount of 1,3-dioxolane in the mixtures, thereby suggesting that ion–ion interactions are weakened with the increase of temperature but strengthened with the increase of 1,3-dioxolane.

The B -coefficient is a measure of effective solvodynamic volume of solvated ions and is governed by size and shape effects of an ion and a structural effect induced by ion–solvent interaction. It is observed from Table 6 that the values of the B -coefficient of different mixtures are positive, thereby suggesting the presence of strong ion–solvent interactions, and these types of interactions are strengthened with a rise in temperature and weakened with an increase of 1,3-dioxolane in the mixtures. These conclusions are in excellent agreement with those drawn from the V_ϕ° values discussed earlier.

It has been reported in a number of studies^{23,24} that dB/dT is a better criterion for determining the structure-making/-breaking

Table 7. Values of $V_2^\circ - V_1^\circ$, $\Delta\mu_1^{of}$, $\Delta\mu_2^{of}$, $T\Delta S_2^{of}$, and ΔH_2^{of} for Ammonium Thiocyanate, Sodium Thiocyanate, and Potassium Thiocyanate in Different Coaqueous (1,3-Dioxolane + Water) Solutions at Different Temperatures

parameters	$T = 298.15$ K	$T = 308.15$ K	$T = 318.15$ K
Ammonium thiocyanate			
10 % by Mass of 1,3-Dioxolane + Water			
$(V_2^\circ - V_1^\circ) \cdot 10^6 / (\text{m}^3 \cdot \text{mol}^{-1})$	8.18	20.39	35.37
$\Delta\mu_1^{of} / (\text{kJ} \cdot \text{mol}^{-1})$	9.70	9.54	9.53
$\Delta\mu_2^{of} / (\text{kJ} \cdot \text{mol}^{-1})$	59.35	74.40	87.42
$T\Delta S_2^{of} / (\text{kJ} \cdot \text{mol}^{-1})$	-418.46	-432.50	-446.53
$\Delta H_2^{of} / (\text{kJ} \cdot \text{mol}^{-1})$	-359.11	-358.09	-359.11
20 % by Mass of 1,3-Dioxolane + Water			
$(V_2^\circ - V_1^\circ) \cdot 10^6 / (\text{m}^3 \cdot \text{mol}^{-1})$	4.38	13.13	25.95
$\Delta\mu_1^{of} / (\text{kJ} \cdot \text{mol}^{-1})$	10.27	10.19	10.17
$\Delta\mu_2^{of} / (\text{kJ} \cdot \text{mol}^{-1})$	44.94	58.92	75.45
$T\Delta S_2^{of} / (\text{kJ} \cdot \text{mol}^{-1})$	-454.77	-470.03	-485.28
$\Delta H_2^{of} / (\text{kJ} \cdot \text{mol}^{-1})$	-409.83	-411.11	-409.83
30 % by Mass of 1,3-Dioxolane + Water			
$(V_2^\circ - V_1^\circ) \cdot 10^6 / (\text{m}^3 \cdot \text{mol}^{-1})$	0.39	6.11	19.31
$\Delta\mu_1^{of} / (\text{kJ} \cdot \text{mol}^{-1})$	10.80	10.72	10.71
$\Delta\mu_2^{of} / (\text{kJ} \cdot \text{mol}^{-1})$	36.57	43.23	50.30
$T\Delta S_2^{of} / (\text{kJ} \cdot \text{mol}^{-1})$	-204.75	-211.62	-218.48
$\Delta H_2^{of} / (\text{kJ} \cdot \text{mol}^{-1})$	-168.18	-168.39	-168.18
Sodium Thiocyanate			
10 % by Mass of 1,3-Dioxolane + Water			
$(V_2^\circ - V_1^\circ) \cdot 10^6 / (\text{m}^3 \cdot \text{mol}^{-1})$	10.20	26.62	41.26
$\Delta\mu_1^{of} / (\text{kJ} \cdot \text{mol}^{-1})$	9.70	9.54	9.53
$\Delta\mu_2^{of} / (\text{kJ} \cdot \text{mol}^{-1})$	63.96	81.29	93.90
$T\Delta S_2^{of} / (\text{kJ} \cdot \text{mol}^{-1})$	-446.33	-461.30	-476.27
$\Delta H_2^{of} / (\text{kJ} \cdot \text{mol}^{-1})$	-382.36	-380.00	-382.36
20 % by Mass of 1,3-Dioxolane + Water			
$(V_2^\circ - V_1^\circ) \cdot 10^6 / (\text{m}^3 \cdot \text{mol}^{-1})$	6.72	20.09	29.57
$\Delta\mu_1^{of} / (\text{kJ} \cdot \text{mol}^{-1})$	10.27	10.20	10.18
$\Delta\mu_2^{of} / (\text{kJ} \cdot \text{mol}^{-1})$	48.64	64.35	83.75
$T\Delta S_2^{of} / (\text{kJ} \cdot \text{mol}^{-1})$	-523.30	-540.85	-558.40
$\Delta H_2^{of} / (\text{kJ} \cdot \text{mol}^{-1})$	-474.65	-476.50	-474.65
30 % by Mass of 1,3-Dioxolane + Water			
$(V_2^\circ - V_1^\circ) \cdot 10^6 / (\text{m}^3 \cdot \text{mol}^{-1})$	1.45	8.12	22.59
$\Delta\mu_1^{of} / (\text{kJ} \cdot \text{mol}^{-1})$	10.81	10.74	10.72
$\Delta\mu_2^{of} / (\text{kJ} \cdot \text{mol}^{-1})$	38.17	47.44	55.97
$T\Delta S_2^{of} / (\text{kJ} \cdot \text{mol}^{-1})$	-265.37	-274.27	-283.17
$\Delta H_2^{of} / (\text{kJ} \cdot \text{mol}^{-1})$	-227.19	-226.83	-227.19
Potassium Thiocyanate			
10 % by Mass of 1,3-Dioxolane + Water			
$(V_2^\circ - V_1^\circ) \cdot 10^6 / (\text{m}^3 \cdot \text{mol}^{-1})$	15.20	31.87	48.75
$\Delta\mu_1^{of} / (\text{kJ} \cdot \text{mol}^{-1})$	9.71	9.55	9.54
$\Delta\mu_2^{of} / (\text{kJ} \cdot \text{mol}^{-1})$	94.46	103.86	114.15
$T\Delta S_2^{of} / (\text{kJ} \cdot \text{mol}^{-1})$	-293.48	-303.32	-313.17
$\Delta H_2^{of} / (\text{kJ} \cdot \text{mol}^{-1})$	-199.02	-199.46	-199.02
20 % by Mass of 1,3-Dioxolane + Water			
$(V_2^\circ - V_1^\circ) \cdot 10^6 / (\text{m}^3 \cdot \text{mol}^{-1})$	10.10	25.34	37.71
$\Delta\mu_1^{of} / (\text{kJ} \cdot \text{mol}^{-1})$	10.30	10.22	10.21
$\Delta\mu_2^{of} / (\text{kJ} \cdot \text{mol}^{-1})$	54.46	65.18	84.74
$T\Delta S_2^{of} / (\text{kJ} \cdot \text{mol}^{-1})$	-451.46	-466.60	-481.75
$\Delta H_2^{of} / (\text{kJ} \cdot \text{mol}^{-1})$	-397.00	-401.42	-397.00
30 % by Mass of 1,3-Dioxolane + Water			
$(V_2^\circ - V_1^\circ) \cdot 10^6 / (\text{m}^3 \cdot \text{mol}^{-1})$	5.16	17.84	29.18
$\Delta\mu_1^{of} / (\text{kJ} \cdot \text{mol}^{-1})$	10.85	10.77	10.76
$\Delta\mu_2^{of} / (\text{kJ} \cdot \text{mol}^{-1})$	45.98	51.51	67.52
$T\Delta S_2^{of} / (\text{kJ} \cdot \text{mol}^{-1})$	-320.99	-331.76	-342.52
$\Delta H_2^{of} / (\text{kJ} \cdot \text{mol}^{-1})$	-275.01	-280.24	-275.01

nature of any solute rather than simply the value of the B -coefficient. It is found from Table 6 that the values of the B -coefficient increase with a rise in temperature (positive dB/dT) suggesting the structure-breaking tendency of all studied thiocyanate salts (viz., NH_4SCN , NaSCN , and KSCN) in different compositions of the 1,3-dioxolane + water mixture. A similar result was reported by some workers^{19,25,26} in the case of the viscosity of lithium and sodium perchlorate in propionic acid + ethanol mixtures. These conclusions are also in excellent agreement with that drawn from the magnitude of $(\delta^2 V_\phi^0 / \delta T^2)_P$ illustrated earlier.

Table 8. Molality m , Sound Velocity u , Adiabatic Compressibility β , Partial Molal Compressibility ϕ_k , Limiting Partial Adiabatic Compressibility ϕ_k° , and Experimental Slope S_k^* of Ammonium Thiocyanate, Sodium Thiocyanate and Potassium Thiocyanate in Different Coaqueous (1,3-Dioxolane + Water) Solutions at $T = 298.15$ K

m	u	$\beta \cdot 10^{10}$	$\phi_k \cdot 10^{10}$	$\phi_k^\circ \cdot 10^{10}$	$S_k^* \cdot 10^{10}$
$\text{mol} \cdot \text{kg}^{-1}$	ms^{-1}	Pa^{-1}	$\text{m}^3 \cdot \text{mol}^{-1} \cdot \text{Pa}^{-1}$	$\text{m}^3 \cdot \text{mol}^{-1} \cdot \text{Pa}^{-1}$	$\text{Pa}^{-1} \cdot \text{kg}^{1/2}$
Ammonium Thiocyanate					
10 % by Mass of 1,3-Dioxolane + Water					
0.00196	1473.7	4.5432	-1.102	-1.215	2.360
0.01370	1490.9	4.4361	-0.949		
0.02545	1505.1	4.3497	-0.857		
0.03720	1513.8	4.2971	-0.734		
0.04896	1525.8	4.2265	-0.706		
0.06072	1531.2	4.1934	-0.628		
20 % by Mass of 1,3-Dioxolane + Water					
0.00194	1485.7	4.4206	-1.680	-1.865	4.511
0.01358	1510.7	4.2730	-1.320		
0.02522	1529.2	4.1674	-1.130		
0.03686	1545.8	4.0755	-1.024		
0.04851	1554.2	4.0289	-0.877		
0.06016	1558.5	4.0033	-0.754		
30 % by Mass of 1,3-Dioxolane + Water					
0.00200	1496.7	4.3161	-1.840	-2.070	5.599
0.01360	1524.6	4.1569	-1.420		
0.02551	1540.9	4.0666	-1.110		
0.03685	1557.8	3.9761	-1.012		
0.04819	1564.7	3.9384	-0.855		
0.06006	1566.5	3.9264	-0.710		
Sodium Thiocyanate					
10 % by Mass of 1,3-Dioxolane + Water					
0.00196	1475.1	4.5343	-1.551	-1.717	3.593
0.01372	1499.6	4.3845	-1.320		
0.02549	1517.0	4.2818	-1.120		
0.03726	1532.7	4.1909	-1.015		
0.04903	1548.4	4.1035	-0.953		
0.06081	1552.4	4.0787	-0.814		
20 % by Mass of 1,3-Dioxolane + Water					
0.00196	1486.2	4.4175	-1.810	-2.045	4.853
0.01376	1515.6	4.2454	-1.500		
0.02555	1537.5	4.1220	-1.290		
0.03735	1550.7	4.0493	-1.080		
0.04916	1566.2	3.9664	-0.991		
0.06097	1568.4	3.9522	-0.827		
30 % by Mass of 1,3-Dioxolane + Water					
0.00208	1498.2	4.3075	-2.170	-2.463	6.957
0.01448	1531.8	4.1176	-1.600		
0.02689	1553.8	3.9985	-1.300		
0.03920	1569.2	3.9172	-1.100		
0.05015	1571.2	3.9043	-0.890		
0.06448	1573.4	3.8895	-0.720		
Potassium Thiocyanate					
10 % by Mass of 1,3-Dioxolane + Water					
0.00196	1477.3	4.5209	-2.230	-2.522	6.892
0.01373	1508.7	4.3308	-1.710		
0.02551	1529.0	4.2130	-1.390		
0.03729	1545.7	4.1187	-1.210		
0.04908	1549.8	4.0932	-0.978		
0.06086	1554.5	4.0643	-0.842		
20 % by Mass of 1,3-Dioxolane + Water					
0.00204	1488.1	4.4064	-2.280	-2.589	7.046
0.01431	1523.1	4.2027	-1.740		
0.02658	1547.6	4.0665	-1.450		
0.03885	1559.8	3.9993	-1.170		
0.05113	1568.7	3.9501	-0.990		
0.06341	1572.6	3.9270	-0.840		
30 % by Mass of 1,3-Dioxolane + Water					
0.00208	1499.2	4.3014	-2.460	-2.805	8.243
0.01448	1537.1	4.0883	-1.800		
0.02690	1559.8	3.9665	-1.420		
0.03920	1573.3	3.8949	-1.160		
0.05015	1574.3	3.8863	-0.930		
0.06449	1578.9	3.8594	-0.770		

The viscosity data have also been analyzed on the basis of transition state theory for the relative viscosity of the solutions as suggested by Feakings et al.²⁷ using eq 7

$$\Delta\mu_2^{of} = \Delta\mu_1^{of} + RT(1000B + V_2^o - V_1^o)/V_1^o \quad (7)$$

$$\phi_k = \phi_k^o + S_k^* m^{1/2} \quad (13)$$

where $\Delta\mu_2^{of}$ is the contribution per mole of the solute to free energy of activation for viscous flow of solutions and $\Delta\mu_1^{of}$ is the free energy of activation per mole of solvent mixture. The values are reported in Table 7. V_1^o is the partial molar volume of the solvent mixture, and V_2^o is the partial molar volume of the solute. $\Delta\mu_1^{of}$ is calculated from

$$\Delta\mu_1^{of} = \Delta G_1^{of} = RT \ln(\eta_o V_1^o / h N_A) \quad (8)$$

where h is Planck's constant and N_A is Avogadro's number. From Table 7, it is seen that $\Delta\mu_1^{of}$ is almost constant at all temperatures and solvent compositions. It means that $\Delta\mu_2^{of}$ is dependent mainly on the values of the viscosity B -coefficients and $(V_2^o - V_1^o)$ terms. $\Delta\mu_2^{of}$ values were positive at all experimental conditions, suggesting that with the rise in temperature and lower concentration of 1,3-dioxolane in the mixtures the process of viscous flow of solutions becomes difficult. So the formation of the transition state becomes less favorable.²⁷ According to Feakings et al.,²⁷ $\Delta\mu_2^{of} > \Delta\mu_1^{of}$ for solutes having positive viscosity B -coefficients indicates stronger solute-solvent interactions, suggesting the formation of a transition state which is accompanied by the rupture and distortion of the intermolecular forces in the solvent structure.²⁷ Equation 9 has been used to calculate the entropy of activation ΔS_2^{of} for solutions.

$$\Delta S_2^{of} = -d(\Delta\mu_2^{of})/dT \quad (9)$$

ΔS_2^{of} has been calculated from the slope of the plots of $\Delta\mu_2^{of}$ versus T by using a least-squares treatment. The enthalpy of activation has been determined by using the following relation²⁷

$$\Delta H_2^{of} = \Delta\mu_2^{of} + T\Delta S_2^{of} \quad (10)$$

The values of ΔS_2^{of} and ΔH_2^{of} are reported in Table 7. They are negative for all studied mixtures at all experimental temperatures. This suggests that the transition state is associated with bond formation and increase in order.

The coefficient of adiabatic compressibility β has been calculated using the relation

$$\beta = 1/\mu^2 \rho \quad (11)$$

where μ is the ultrasonic velocity and ρ is the density of the solution.

The apparent molal adiabatic compressibility ϕ_k of the solution was computed from the relation

$$\phi_k = \beta M / \rho + 1000(\beta \rho_o - \beta_o \rho) / m \rho \rho_o \quad (12)$$

where β and β_o are the adiabatic compressibility of solution and solvent, respectively, and m is the molal concentration of the solution.

The limiting apparent molal adiabatic compressibilities ϕ_k^o were obtained by extrapolating the plots of ϕ_k versus $m^{1/2}$ of the solution to zero concentration by a computerized least-squares method

where S_k^* is the experimental slope.

The values of m , μ , β , ϕ_k , ϕ_k^o , and S_k^* for all the studied mixtures at 298.15 K are determined and reported in Table 8.

It is evident from Table 8 that all the mixtures investigated here have negative apparent molal adiabatic compressibility ϕ_k^o and positive limiting experimental slopes S_k^* . These results can be interpreted in terms of the loss of compressibility of the 1,3-dioxolane + water mixture due to electrostrictive forces in the vicinity of the ions. The same conclusion was obtained in the case of studies on sound velocities of some alkali metal halides in THF + H₂O mixtures.^{19,28}

Conclusion

The extensive study of the densities, viscosities, and speeds of sound of different thiocyanates in various mass fractions of the solvent mixture of 1,3-dioxolane and water at different temperatures reveals the characteristics and structural properties prevalent in the solutions. In summary, V_ϕ^o and viscosity B -coefficient values for the different thiocyanates indicate the presence of strong ion-solvent interactions, and these interactions are further strengthened with a rise in temperature and with a decrease in the amount of 1,3-dioxolane in the mixtures. It also indicates that all studied mixtures act as structure breakers.

List of Symbols

ρ	Density of solution
ρ_o	Density of solvent
η	Viscosity of solution
η_o	Viscosity of solvent
c	Molar concentration of solution
m	Molal concentration of solution
ΔS_2^{of}	Entropy of activation
ΔH_2^{of}	Enthalpy of activation
μ	Speed of sound of solution
μ_o	Speed of sound of solvent
β	Adiabatic compressibility of solution
β_o	Adiabatic compressibility of solvent
ϕ_k	Apparent molal adiabatic compressibility
ϕ_k^o	Limiting apparent molal adiabatic compressibility
S_k^*	Experimental slope
ϕ_v	Apparent molar volume
ϕ_v^o	Limiting apparent molar volume
S_v^*	Experimental slope
M	Molecular weight of solute
ϕ_E	Apparent molar expansibility
ϕ_E^o	Limiting apparent molar expansibility
h	Planck's constant
N_A	Avogadro's number
1,3-DO	1,3-dioxolane
H ₂ O	Water

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