Apparent Molar Volumes and Isentropic Compressibilities of Benzene Sulfonates and Naphthalene Sulfonates in Aqueous Solutions at (293.15, 303.15, 313.15, 323.15, and 333.15) K

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Densities and speeds of sound for aqueous solutions of sodium benzene sulfonate, sodium *p*-toluene sulfonate, disodium 1,3-benzene disulfonate, sodium 1-naphthalene sulfonate, and disodium 1,5-naphthalene disulfonate were accurately measured at various concentrations and at (293.15, 303.15, 313.15, 323.15, and 333.15) K. These data were utilized in determining apparent molar volumes, V_Φ, and apparent molar isentropic compressibilities, $K_{S\Phi}$. V_Φ and $K_{S\Phi}$ values were plotted against concentration according to equations based on the Debye−Hückel theory, and the corresponding infinite dilution values (V^0_Φ and $K^0_{S\Phi}$) were determined by extrapolation to zero concentration. Properties at infinite dilution were interpreted in terms of solute−water interactions. The temperature dependence of volumetric data provided the apparent molar isobaric expansivities of benzene and naphthalene sulfonates. A comparison of V^0_Φ and $K^0_{S\Phi}$ values for certain pairs of systematically chosen benzene and naphthalene sulfonates provided important information about the effects of certain hydrophobic or hydrophilic groups in the structures on the solution behavior of these sulfonates.

Introduction

Benzene and naphthalene sulfonates are widely used in the preparation of azo dyestuffs, pharmaceuticals, tanning agents, catalysts, pesticides, ion exchange resins, optical brighteners, wetting and finishing agents, plasticizers, and chemicals for organic synthesis.[1−3] They are highly soluble in water and are found as pollutants in waste waters of the industries where they are used heavily. The interaction of these compounds with water plays an important role in their removal studies from waste waters. Most of the removal works involve adsorption or electrosorption of these compounds onto various adsorbents, primarily activated carbon.[4−9] There is a kind of competition between water and adsorbent for the adsorbate. The size of the compounds is important in penetrating into the pores of the adsorbent. They may be adsorbed in hydrated or anhydrated form. These are all determined by the behavior of the solute in solution, i.e., by solute−solvent interactions. Information about such interactions is important not only for their adsorption or electrosorption but also for various reactions they undergo during their industrial usage. Apparent molar volumes, apparent molar isentropic compressibilities, and apparent molar expansivities are important tools in determining the solution behavior of solutes and are being studied for various compounds.[10−14] Some correlations are explored between these volumetric properties and the adsorption behavior of certain pollutants.[15] There is not much work reported on volumetric and compressibility behavior of benzene and naphthalene sulfonates in the literature. The purpose of the present study is to investigate the aqueous solution behavior of benzene and naphthalene sulfonates and their derivatives by determining their apparent molar volumes, isentropic compressibilities, and expansivities through accurate density and speed of sound measurements at various temperatures.

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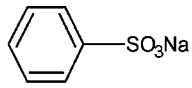
Experimental Section

Materials. Sodium benzene sulfonate (NaBS), sodium *p*-toluene sulfonate (NaTS), and disodium 1,5-naphthalene disulfonate (Na_2NDS) were obtained from Aldrich, while disodium 1,3-benzene disulfonate (Na_2BDS) and sodium 1-naphthalene sulfonate (NaNS) were obtained from the ABCR company. The purities of these compounds were higher than 95 %, and the compounds were used without further purification. The names, structures, and abbreviations of the compounds are given in Figure 1. The solutions were prepared at desired molalities by weighing first an empty volumetric flask (usually 50 mL), then a flask with the solute, and finally a flask containing the solute and solvent (H_2O), using a Chyo JL-200 model balance, sensitive to ± 0.1 mg.

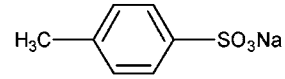
Density and Speed of Sound Measurements. Densities and speeds of sound were measured by an Anton Paar DSA 5000 model high precision vibrating tube digital densimeter and speed of sound measuring device, with automatic viscosity corrections. The instrument has a built-in thermostat to maintain the temperature between (0 and 70) °C with a precision of ± 0.005 °C. The calibration of the instrument was made with degassed and bidistilled water by measuring its density and speed of sound at 20 °C and comparing them with reference values given in the instruction manual of the instrument. The uncertainty of measurements was $\pm\ 5\cdot10^{-6}$ g·cm^{-3} for density and ± 0.05 m·s^{-1} for speed of sound. The instrument required a liquid volume of about 2.5 mL and measured the density and speed of sound simultaneously after a thermal equilibration period of about (5 to 10) min.

Density and speed of sound measurements were carried out for aqueous solutions of benzene and naphthalene sulfonates at various concentrations and at five temperatures: (293.15, 303.15,

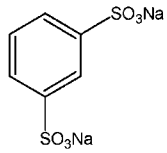
10.1021/je9005486
Published on Web 12/09/2009



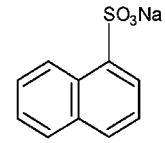
Sodium benzene sulfonate (NaBS)



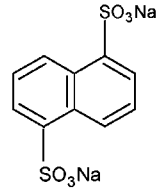
Sodium p-toluene sulfonate (NaTS)



Disodium 1,3-benzene disulfonate (Na_2BDS)



Sodium naphthalene sulfonate (NaNS)



Disodium 1,5-naphthalene disulfonate (Na_2NDS)

Figure 1. Names, structures, and abbreviations of benzene and naphthalene sulfonates.

313.15, 323.15, and 333.15) K. The measured densities and speeds of sound were utilized in determining apparent molar volumes and isentropic compressibilities as described in the following section.

Treatment of Data. Apparent molar volumes, V_Φ, were determined from the following equation[16]

$$V_\Phi = [(\rho_0 - \rho)/(C\rho_0)] + M_2/\rho_0 \quad (1)$$

where ρ_0 and ρ are densities of water and solution, respectively. C is the molarity, and M_2 is the molecular weight of solute.

Apparent molar volumes at infinite dilution, V^0_Φ, were determined by treating the V_Φ versus C data according to the Redlich and Meyer[17] equation

$$V_\Phi = V^0_\Phi + S_v\sqrt{C} + b_vC \quad (2)$$

where S_v is known as the Debye−Hückel limiting slope and b_v is an experimentally determined parameter. S_v depends on the valency of solute, not on its nature, and is given by the following equation[17]

$$S_v = kw^{3/2} \quad (3)$$

where k is the limiting slope and w is the so-called valency factor. The valency factor has been defined by Redlich and Meyer[17] with the following equation

$$w = 0.5\sum \nu_i z_i^2 \quad (4)$$

where ν_i and z_i are the number and charge of each ion constituting the electrolyte. Redlich and Meyer developed the following polynomial equation for the limiting slope, k, in terms of temperature, T, in kelvin between (273.15 and 343.15) K[16]

$$k = 1.4447 + 1.6799\cdot10^{-2}(T - 273.15) - 8.4055\cdot10^{-6}(T - 273.15)^2 + 5.5153\cdot10^{-7}(T - 273.15)^3 \quad (5)$$

Debye−Hückel limiting slopes for 1:1 and 2:2 electrolytes at the temperatures of interest of this study, calculated using eqs 3 and 5, are given in Table 1. The slopes given in this table are limited to 1:1 and 2:2 type electrolytes since the benzene and naphthalene sulfonates under study are either of these two types. Equation 2 can be rearranged to obtain a linear equation as follows

$$V_\Phi - S_v\sqrt{C} = V^0_\Phi + b_vC \quad (6)$$

according to which plots of $(V_\Phi - S_v\sqrt{C})$ versus C data using an appropriate S_v value are expected to give a straight line with a slope of b_v and an intercept of V^0_Φ.

Apparent molar isobaric expansivities at infinite dilution, E^0_Φ, can be obtained on the basis of the following equation[18]

$$E^0_\Phi = (\partial V^0_\Phi/\partial T)_P \quad (7)$$

where T is the temperature and P is the pressure. According to eq 7, the slope of V^0_Φ versus T curve at any T gives E^0_Φ. A V^0_Φ versus T plot is linear over a certain T range which implies that E^0_Φ is constant over that T range and given by the slope of that line.

Apparent molar isentropic compressibilities, $K_{S\Phi}$, were obtained from the following equation[19]

$$K_{S\Phi} = [(\beta_S - \beta^o_S)/m\rho_0] + \beta_S V_\Phi \quad (8)$$

where β_S and β^o_S are isentropic compressibilities of solution and water, respectively; V_Φ is the apparent molar volume; m is the molality; and ρ_0 is the density of water. It should be noted that the availability of the Debye−Hückel limiting slope values only at the molarity scale (at molality scale they are available only for 1:1 electrolytes[20]) necessitated the use of molarity for determining apparent molar volumes. However, since the

Table 1. Debye−Hückel Limiting Slopes for 1:1 and 2:2 Electrolytes at Various Temperatures

	$S_v/(cm^3\cdot mol^{-3/2}\cdot L^{1/2})$	
T/K	1:1	2:2
293.15	1.7817	40.315
303.15	1.9560	44.259
313.15	2.1385	48.389
323.15	2.3326	52.781
333.15	2.5415	57.508

Table 2. Densities and Speeds of Sound for Aqueous Solutions of Benzene and Naphthalene Sulfonates at Various Temperatures

	m	ρ	u	ρ	u	ρ	u	ρ	u	ρ	u
compound	(mol·kg^{-1})	(g·cm^{-3})	(m·s^{-1})	(g·cm^{-3})	(m·s^{-1})	(g·cm^{-3})	(m·s^{-1})	(g·cm^{-3})	(m·s^{-1})	(g·cm^{-3})	(m·s^{-1})
		T = 293.15 K		T = 303.15 K		T = 313.15 K		T = 323.15 K		T = 333.15 K	
NaBS	0.0000	0.998240	1482.55	0.995681	1509.29	0.992248	1529.03	0.988070	1542.74	0.983232	1551.18
	0.0504	1.002280	1488.55	0.999640	1514.36	0.996144	1533.42	0.991910	1546.61	0.987030	1554.54
	0.1020	1.006285	1494.24	1.003564	1519.35	1.000001	1537.80	0.995717	1550.39	0.990794	1557.90
	0.1506	1.010024	1499.81	1.007224	1524.08	1.003601	1541.88	0.999263	1553.97	0.994303	1560.93
	0.2017	1.013889	1505.41	1.011014	1528.91	1.007328	1546.05	1.002938	1557.57	0.997935	1564.07
	0.2517	1.017615	1510.65	1.014660	1533.49	1.010912	1550.02	1.006475	1560.99	1.001426	1567.07
	0.3011	1.021268	1515.98	1.018241	1538.01	1.014430	1553.91	1.009945	1564.37	1.004856	1569.98
	0.3512	1.024932	1521.14	1.021825	1542.49	1.017954	1557.79	1.013422	1567.70	1.008291	1572.87
	0.4029	1.028650	1526.26	1.025474	1546.96	1.021541	1561.69	1.016956	1571.08	1.011784	1575.78
	0.4992	1.035484	1535.89	1.032163	1555.18	1.028114	1568.77	1.023432	1577.23	1.018186	1581.07
NaTS	0.0000	0.998240	1482.55	0.995681	1509.29	0.992248	1529.03	0.988070	1542.74	0.983232	1551.18
	0.0508	1.002294	1489.55	0.999463	1515.23	0.996134	1534.18	0.991895	1547.22	0.987007	1555.04
	0.1007	1.006199	1496.30	1.003460	1521.10	0.999881	1539.24	0.995580	1551.55	0.990644	1558.72
	0.1518	1.010152	1502.72	1.007320	1526.57	1.003669	1543.96	0.999310	1555.64	0.994330	1562.29
	0.2006	1.013877	1508.92	1.010958	1531.85	1.007236	1548.49	1.002819	1559.53	0.997789	1565.62
	0.2498	1.017551	1514.88	1.014550	1536.96	1.010753	1552.92	1.006281	1563.32	1.001201	1568.88
	0.3016	1.021362	1520.87	1.018268	1542.21	1.014403	1557.37	1.009868	1567.17	1.004740	1572.21
	0.3496	1.024889	1526.57	1.021714	1547.03	1.017783	1561.52	1.013191	1570.73	1.008018	1575.18
	0.3976	1.028357	1531.97	1.025097	1551.70	1.021098	1565.53	1.016453	1574.14	1.011233	1578.09
	0.4991	1.035528	1543.14	1.032101	1561.27	1.027964	1573.72	1.023204	1581.18	1.017888	1584.12
Na_2BDS	0.0000	0.998240	1482.55	0.995681	1509.29	0.992248	1529.03	0.988070	1542.74	0.983232	1551.18
	0.0502	1.006388	1489.89	1.003706	1515.67	1.000182	1534.76	0.995933	1547.97	0.991049	1555.94
	0.1001	1.014177	1496.82	1.011378	1521.83	1.007764	1540.31	1.003453	1552.98	0.998523	1560.55
	0.1533	1.022346	1503.91	1.019425	1528.19	1.015717	1546.06	1.011337	1558.19	1.006270	1565.35
	0.1997	1.029343	1510.19	1.026319	1533.72	1.022536	1550.97	1.018096	1562.68	1.013068	1569.48
	0.2494	1.036683	1516.65	1.033553	1539.50	1.029689	1556.15	1.025188	1567.38	1.020117	1573.77
	0.3001	1.044508	1524.10	1.041278	1546.15	1.037336	1562.06	1.032770	1572.78	1.027221	1578.74
	0.3495	1.051286	1529.65	1.047950	1551.03	1.043930	1566.52	1.039307	1576.78	1.034144	1582.36
	0.3998	1.058634	1536.44	1.055248	1557.11	1.051150	1571.99	1.046468	1581.74	1.041263	1586.88
	0.4987	1.072371	1548.52	1.068751	1567.88	1.064505	1581.70	1.059710	1590.60	1.054419	1595.10
NaNS	0.0000	0.998240	1482.55	0.995681	1509.29	0.992248	1529.03	0.988070	1542.74	0.983232	1551.18
	0.0251	1.000628	1486.17	0.998022	1512.24	0.994547	1531.56	0.990337	1544.89	0.985467	1552.95
	0.0503	1.002916	1489.61	1.000260	1515.17	0.996743	1534.07	0.992491	1547.11	0.987601	1554.89
	0.0748	1.005115	1492.77	1.002403	1517.94	0.998850	1536.41	0.994569	1549.07	0.989647	1556.54
	0.0994	1.007307	1495.84	1.004550	1520.57	1.000953	1538.72	0.996635	1551.08	0.991692	1558.25
	0.1249	1.009575	1499.17	1.006766	1523.40	1.003128	1541.12	0.998779	1553.12	0.993801	1560.02
	0.1496	1.011758	1502.28	1.008901	1526.05	1.005223	1543.41	1.000838	1555.07	0.995835	1561.69
	0.1703	1.013542	1504.74	1.010646	1528.22	1.006931	1545.27	1.002520	1556.68	0.997491	1563.06
	0.2001	1.016147	1508.36	1.013188	1531.34	1.009428	1547.95	1.004977	1558.98	0.999916	1565.02
	0.2245	1.018241	1511.22	1.015237	1533.82	1.011437	1550.08	1.006954	1560.79	1.001866	1566.60
Na_2NDS	0.0000	0.998240	1482.55	0.995681	1509.29	0.992248	1529.03	0.988070	1542.74	0.983232	1551.18
	0.0500	1.006983	1491.21	1.004289	1516.91	1.000754	1535.86	0.996493	1548.94	0.991597	1556.80
	0.0750	1.011226	1495.43	1.008466	1520.62	1.004880	1539.18	1.000580	1551.94	0.995655	1559.53
	0.1001	1.015430	1499.71	1.012605	1524.36	1.008968	1542.51	1.004631	1554.92	0.999675	1562.24
	0.1261	1.019782	1503.92	1.016887	1528.15	1.013200	1545.89	1.008820	1557.99	1.003836	1565.03
	0.1500	1.023700	1507.79	1.020748	1531.59	1.017013	1548.97	1.012602	1560.73	1.007590	1567.52
	0.1987	1.031581	1515.75	1.028506	1538.60	1.024680	1555.19	1.020198	1566.31	1.015131	1572.59
	0.2426	1.038549	1522.73	1.035373	1544.72	1.031464	1560.68	1.026917	1571.26	1.021802	1577.12
	0.2865	1.045388	1529.52	1.042108	1550.75	1.038122	1566.08	1.033513	1576.08	1.028349	1581.44
	0.3370	1.053150	1537.13	1.049758	1557.56	1.045682	1572.16	1.041004	1581.57	1.035786	1586.45

densities of solutions are measured accurately, it is always possible to convert m and C to each other. Isentropic compressibilities β_S and β^o_S were obtained from eqs 9 and 10, respectively, using the measured speeds of sound u_0 for water and u for solution

$$\beta^o_S = 1/(u_0^2\rho_0) \quad (9)$$

$$\beta_S = 1/(u^2\rho) \quad (10)$$

So, the determination of apparent molar isentropic compressibilities involved the usage of measured densities and speeds of sound in eqs 1, 9, 10, and then 8, successively.

For electrolytes, the dependence of $K_{S\Phi}$ on concentration is treated, on the basis of Debye−Hückel theory, according to the following equation

$$K_{S\Phi} = K^0_{S\Phi} + S_{SK}\sqrt{m} \quad (11)$$

where S_{SK} is the limiting slope and $K^0_{S\Phi}$ is the apparent molar isentropic compressibility at infinite dilution. Linear regression analysis of $K_{S\Phi}$ versus $\sqrt{m}$ data yields the two parameters $K^0_{S\Phi}$ and S_{SK} from the intercept and slope, respectively.

Results

Densities and speeds of sound of benzene and naphthalene sulfonates at varying molalities measured at (293.15, 303.15, 313.15, 323.15, and 333.15) K in aqueous solutions are given in Table 2. The available literature data[21,22] for densities of NaBS and Na_2BDS at 298.15 K are given in graphical form in Figure 2 together with the present data for comparison.

Apparent molar volumes were calculated from the measured densities through eq 1. Then, ($V_\Phi - S_v\sqrt{C}$) values were calculated at each temperature using the appropriate S_v value from Table 1 and plotted against C. The data were regressed linearly according to eq 6 to determine the V^0_Φ values and the b_v parameters. Typical plots for NaNS are given in Figure 3. Similar plots were also obtained for other sulfonates.

Apparent molar isentropic compressibilities were calculated from the measured densities and speeds of sound using eqs 9,

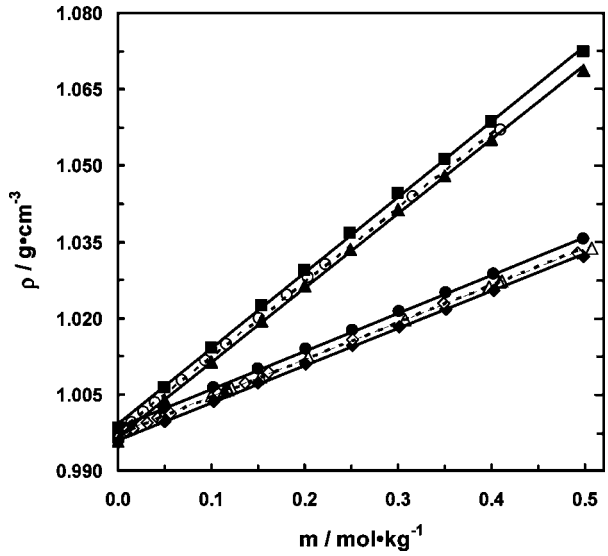


Figure 2. Densities of aqueous NaBS solutions from this study at ●, 293.15 K and at ◆, 303.15 K, from Perron and Desnoyers[21] at △, 298.15 K, and from Sanchez and Chriss[22] at ◇, 298.15 K, and of aqueous Na_2BDS solutions from this study at ■, 293.15 K and at ▲, 303.15 K and from Perron and Desnoyers[21] at ○, 298.15 K.

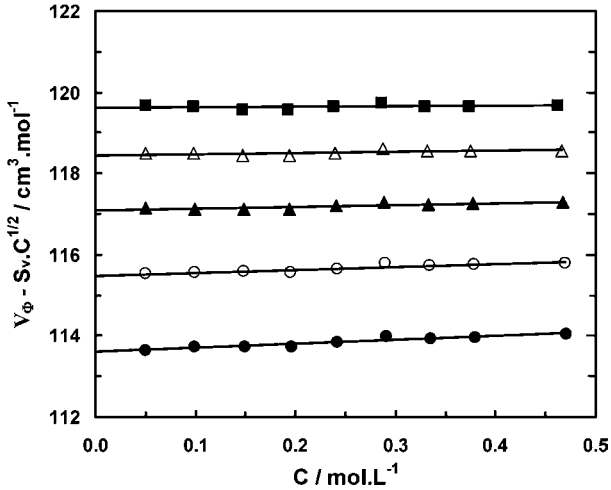


Figure 3. Plots of ($V_\Phi - S_v\sqrt{C}$) vs molarity for NaNS in water at ●, 293.15 K; ○, 303.15 K; ▲, 313.15 K; △, 323.15 K; and ■, 333.15 K.

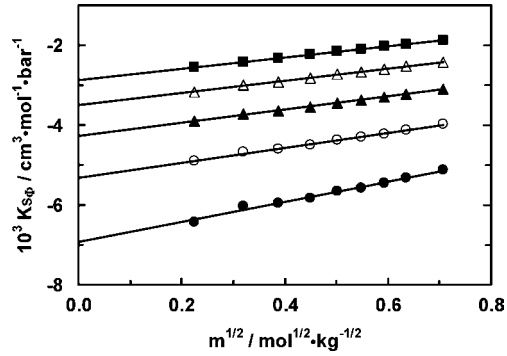


Figure 4. Plots of $K_{S\Phi}$ vs molality$^{1/2}$ for NaBS in water at ●, 293.15 K; ○, 303.15 K; ▲, 313.15 K; △, 323.15 K; and ■, 333.15 K.

10, 1, and then 8 successively. They were then plotted against the square root of molality. The data were regressed linearly according to eq 11 to determine $K^0_{S\Phi}$ values and S_{SK} parameters. Typical plots for NaBS are given in Figure 4. Similar plots were also obtained for other sulfonates.

V^0_Φ, b_v, $K^0_{S\Phi}$, and S_{SK} values, together with coefficients of determination (R^2), for benzene and naphthalene sulfonates in aqueous solution at various temperatures are collectively given in Table 3.

Discussion

Temperature Dependence of V^0_Φ and $K^0_{S\Phi}$. Plots of V^0_Φ as a function of temperature for benzene and naphthalene sulfonates are shown in Figure 5. The fairly good linearity observed in these plots indicates that the apparent molar isobaric expansivity at infinite dilution, E^0_Φ, is constant within the studied temperature range and is given by the slope of the line for each sulfonate species according to eq 7. E^0_Φ values are all positive and are greater for 1:1 type sulfonates than for 2:2 type sulfonates. If one wants to correlate the E^0_Φ values with the structures of all the sulfonates studied, the following general conclusion can be arrived: E^0_Φ values increase with decreasing hydrophilic/hydrophobic ratio or with increasing hydrophobic surface in the structure.

$K^0_{S\Phi}$ values are also increasing with temperature for all the sulfonates studied, although they are all negative (Table 3). Negative $K^0_{S\Phi}$ values are explained by the electrostriction of water under the ionic field in the primary and secondary hydration shells. The increase in isentropic compressibility with temperature is a consequence of positive isobaric expansivity (Table 4).

Effects of Structural Factors on Infinite Dilution Properties. Interesting results were obtained when a comparison is made between infinite dilution values (V^0_Φ and $K^0_{S\Phi}$) of certain pairs of the compounds studied, leading to some generalization about the volume and compressibility behavior in relation to certain groups in the structures. The selected pairs are NaTS−NaBS, Na_2BDS−NaBS, Na_2NDS−NaNS, NaNS−NaBS, and Na_2NDS−Na_2BDS. The differences in V^0_Φ, ΔV^0_Φ, and in $K^0_{S\Phi}$, $\Delta K^0_{S\Phi}$ were calculated by subtracting the property (V^0_Φ or $K^0_{S\Phi}$) of the second member of the pair from that of the first member of the pair at each temperature and are recorded in Table 5. The results for each pair can be interpreted in the following ways.

NaTS−NaBS: The structural difference between these two compounds is that −H in the para position of NaBS is replaced by $-CH_3$ in NaTS. Therefore, there is an increase in V^0_Φ in going from NaBS to NaTS (positive ΔV^0_Φ). Furthermore, this volume difference is increasing regularly with temperature (Table 5). The increase in ΔV^0_Φ with temperature can be explained by the higher hydrophobicity of NaTS. The $K^0_{S\Phi}$ value of NaTS is less than that of NaBS at low temperatures (negative $\Delta K^0_{S\Phi}$) again due to its higher hydrophobicity. The so-called "icelike" structure of water around hydrophobic solutes is considered to be less compressible. However, at higher temperatures, this trend is reversed due to melting of the icelike structure, and $\Delta K^0_{S\Phi}$ takes even positive values.

Na_2BDS−NaBS: Here, the structural difference is that −H in the meta position of NaBS is replaced by $-SO_3Na$ in Na_2BDS. Thus, there is an increase in V^0_Φ in going from NaBS to Na_2BDS (positive ΔV^0_Φ). However, this volume difference is decreasing regularly with temperature (Table 5) which can be explained by the higher hydrophilicity of Na_2BDS than that of NaBS, acquired by the second $-SO_3Na$ group in Na_2BDS. The $K^0_{S\Phi}$ of Na_2BDS is less than that of NaBS (negative $\Delta K^0_{S\Phi}$, Table 5) due to its increased ionic character. Electrostricted water under the ionic field is less compressible than ordinary water. $\Delta K^0_{S\Phi}$ is increasing with temperature, probably due to

Table 3. V^0_Φ, b_v, $K^0_{S\Phi}$, and S_{SK} Values for Benzene and Naphthalene Sulfonates in Aqueous Solutions

compound	T (K)	V^0_Φ ($cm^3 \cdot mol^{-1}$)	b_v ($cm^3 \cdot mol^{-2} \cdot L$)	R^2	$10^3\ K^0_{S\Phi}$ ($cm^3 \cdot mol^{-1} \cdot bar^{-1}$)	$10^3\ S_{SK}$ ($cm^3 \cdot mol^{-3/2} \cdot kg^{1/2} \cdot bar^{-1}$)	R^2
NaBS	293.15	99.4 ± 0.1	−5.1 ± 0.5	0.9340	−6.93 ± 0.05	2.5 ± 0.1	0.9896
	303.15	101.2 ± 0.1	2.3 ± 0.5	0.7259	−5.33 ± 0.02	1.89 ± 0.05	0.9961
	313.15	102.5 ± 0.2	2.1 ± 0.5	0.6870	−4.27 ± 0.01	1.64 ± 0.03	0.9980
	323.15	103.7 ± 0.1	1.8 ± 0.5	0.6531	−3.51 ± 0.01	1.54 ± 0.03	0.9979
	333.15	104.7 ± 0.1	1.7 ± 0.5	0.6283	−2.87 ± 0.00	1.42 ± 0.01	0.9998
NaTS	293.15	113.6 ± 0.0	1.0 ± 0.1	0.9127	−7.69 ± 0.05	3.2 ± 0.1	0.9921
	303.15	115.5 ± 0.0	0.7 ± 0.1	0.8687	−5.84 ± 0.07	2.5 ± 0.1	0.9812
	313.15	117.1 ± 0.0	0.5 ± 0.1	0.7118	−4.58 ± 0.05	2.1 ± 0.1	0.9836
	323.15	118.4 ± 0.0	0.4 ± 0.1	0.4303	−3.61 ± 0.03	1.88 ± 0.07	0.9914
	333.15	119.6 ± 0.0	0.1 ± 0.2	0.1063	−2.79 ± 0.03	1.65 ± 0.05	0.9933
Na_2BDS	293.15	111.2 ± 0.4	−33 ± 1	0.9863	−11.8 ± 0.1	4.56 ± 0.02	0.9828
	303.15	112.8 ± 0.5	−38 ± 2	0.9869	−9.90 ± 0.01	3.6 ± 0.2	0.9807
	313.15	113.7 ± 0.5	−43 ± 2	0.9872	−8.72 ± 0.09	3.2 ± 0.2	0.9813
	323.15	114.1 ± 0.6	−48 ± 2	0.9870	−7.90 ± 0.09	3.0 ± 0.2	0.9779
	333.15	114.1 ± 0.4	−53 ± 2	0.9937	−7.30 ± 0.05	2.8 ± 0.1	0.9899
NaNS	293.15	135.2 ± 0.5	0.4 ± 5	0.0014	−7.7 ± 0.1	4.7 ± 0.1	0.9722
	303.15	137.4 ± 0.5	13 ± 4	0.6283	−5.46 ± 0.04	3.03 ± 0.041	0.9898
	313.15	139.2 ± 0.5	13 ± 4	0.6273	−4.13 ± 0.05	2.59 ± 0.05	0.9831
	323.15	140.8 ± 0.6	13 ± 4	0.5948	−3.11 ± 0.04	2.29 ± 0.04	0.9850
	333.15	142.2 ± 0.5	13 ± 4	0.6195	−2.13 ± 0.04	1.74 ± 0.04	0.9718
Na_2NDS	293.15	148.5 ± 0.2	−35 ± 1	0.9979	−12.6 ± 0.0	5.18 ± 0.04	0.9975
	303.15	150.4 ± 0.3	−40 ± 1	0.9936	−10.5 ± 0.0	4.27 ± 0.03	0.9982
	313.15	151.7 ± 0.3	−46 ± 2	0.9942	−9.08 ± 0.02	3.85 ± 0.02	0.9994
	323.15	152.6 ± 0.4	−52 ± 2	0.9926	−8.11 ± 0.01	3.65 ± 0.01	0.9997
	333.15	152.9 ± 0.4	−58 ± 2	0.9888	−7.34 ± 0.01	3.39 ± 0.01	0.9994

the increase in compressibility of less compressible icelike water around the more hydrophobic NaBS at higher temperatures upon melting.

Na_2NDS−NaNS: The structural difference between these compounds is almost the same as in the previous pair. There is a replacement of −H in NaNS by $-SO_3Na$ in Na_2NDS. Thus, there is again an increase in V^0_Φ in going from NaNS to Na_2NDS (positive ΔV^0_Φ), and the magnitude of ΔV^0_Φ is decreasing with temperature (Table 5), a consequence of the higher hydrophilicity of Na_2NDS with two sulfonate groups than that of NaNS. The comparison of $K^0_{S\Phi}$ of these two compounds is interesting because in Na_2NDS there are two ionic groups causing a decrease in compressibility due to electrostriction, while in NaNS there is more hydrophobic surface, thus more water around it in an icelike state, again causing a decrease in compressibility. The negative values of $\Delta K^0_{S\Phi}$ (Table 5) indicate that the decrease in compressibility due to electrostriction of water in Na_2NDS is more important than that due to hydrophobicity in NaNS. $\Delta K^0_{S\Phi}$ values are becoming more negative with increasing temperature because the water in the icelike state around NaNS is melting with temperature causing an increase in its compressibility.

NaNS−NaBS: The structural difference between these two compounds is that in NaNS a second benzene ring is attached to NaBS, by replacing the two −H groups in consecutive ortho

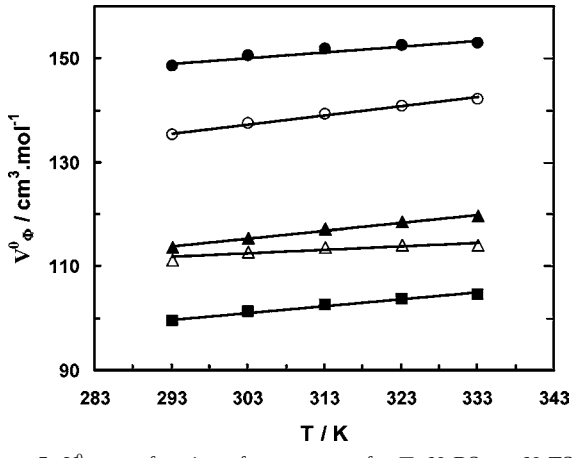


Figure 5. V^0_Φ as a function of temperature for ■, NaBS; ▲, NaTS; △, Na_2BDS; ○, NaNS; and ●, Na_2NDS in water.

Table 4. E^0_Φ Values and Linear Regression Coefficients of V^0_Φ versus T Data

compound	E^0_Φ ($cm^3 \cdot mol^{-1} \cdot K^{-1}$)	R^2
NaBS	0.1303	0.9847
NaTS	0.1493	0.9911
Na_2BDS	0.0697	0.8388
NaNS	0.1742	0.9918
Na_2NDS	0.1105	0.9215

Table 5. ΔV^0_Φ and $\Delta K^0_{S\Phi}$ Values for Some Benzene and Naphthalene Sulfonate Pairs at Various Temperatures

pair	T K	ΔV^0_Φ $cm^3 \cdot mol^{-1}$	$\Delta K^0_{S\Phi}$ $10^3\ cm^3 \cdot mol^{-1} \cdot bar^{-1}$
NaTS−NaBS	293.15	14.2 ± 0.1	−0.76 ± 0.07
	303.15	14.3 ± 0.1	−0.51 ± 0.07
	313.15	14.6 ± 0.2	−0.31 ± 0.05
	323.15	14.7 ± 0.1	0.10 ± 0.04
	333.15	14.9 ± 0.2	0.08 ± 0.03
Na_2BDS−NaBS	293.15	11.8 ± 0.4	−4.9 ± 0.1
	303.15	11.6 ± 0.5	−4.57 ± 0.03
	313.15	11.2 ± 0.5	−4.45 ± 0.09
	323.15	10.4 ± 0.6	−4.39 ± 0.09
	333.15	9.4 ± 0.5	−4.43 ± 0.05
Na_2NDS−NaNS	293.15	13.3 ± 0.5	−4.9 ± 0.1
	303.15	13.0 ± 0.6	−5.04 ± 0.05
	313.15	12.5 ± 0.6	−4.95 ± 0.05
	323.15	11.8 ± 0.7	−5.00 ± 0.04
	333.15	10.7 ± 0.6	−5.21 ± 0.04
NaNS−NaBS	293.15	35.8 ± 0.5	−0.8 ± 0.1
	303.15	36.2 ± 0.5	−0.13 ± 0.05
	313.15	36.7 ± 0.5	0.14 ± 0.04
	323.15	37.1 ± 0.6	0.40 ± 0.04
	333.15	37.3 ± 0.5	0.74 ± 0.04
Na_2NDS−Na_2BDS	293.15	37.2 ± 0.5	−0.8 ± 0.1
	303.15	37.6 ± 0.5	−0.60 ± 0.03
	313.15	38.0 ± 0.6	−0.36 ± 0.01
	323.15	38.5 ± 0.7	−0.21 ± 0.09
	333.15	38.8 ± 0.6	−0.04 ± 0.06

and para positions of the $-SO_3Na$ group. This highly hydrophobic benzene group causes a large increase in V^0_Φ in going from NaBS to NaNS resulting in positive ΔV^0_Φ values. These ΔV^0_Φ values increase with temperature (Table 5) due to the higher hydrophobicity of NaNS. The increase in $\Delta K^0_{S\Phi}$ with temperature is also associated with higher hydrophobicity of NaNS.

$Na_2NDS-Na_2BDS$: There are two $-SO_3Na$ groups in both compounds. The difference in structures is that, on the whole, two $-H$ groups in Na_2BDS are replaced by a second benzene ring in Na_2NDS similar to the case in the previous pair of compounds. Therefore, there is an increase in V^0_Φ in going from Na_2BDS to Na_2NDS resulting in positive ΔV^0_Φ values. The magnitudes of these ΔV^0_Φ values are close to those of the previous pair, and they increase with temperature due to higher hydrophobicity of the extra benzene ring in Na_2NDS. The increase in $\Delta K^0_{S\Phi}$ with temperature is again associated with the increased hydrophobicity in Na_2NDS by the additional benzene ring compared to Na_2BDS.

Conclusions

Substitution of certain groups such as $-CH_3$, $-SO_3Na$, or a benzene ring to a benzene or naphthalene sulfonate causes a definite increase in volume. The change of this increase with temperature seems to be dependent on the extra hydrophobicity or hydrophilicity provided to the molecule by such groups. The change in volume increases with temperature for substituents causing an increase in hydrophobicity ($-CH_3$ or benzene) and decreases with temperature for substituents causing an increase in hydrophilicity ($-SO_3Na$). Compressibility data support these findings. A lowering in compressibility due to electrostriction is more important than that due to hydrophobicity of the solute. The apparent molar isobaric expansivity at infinite dilution for the sulfonates studied is almost constant over the temperature range (293.15 to 333.15) K.

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Received for review June 30, 2009. Accepted November 27, 2009. This paper was produced from a project (number: 2003.01.0300.009) supported by The Scientific Research Projects Coordination Unit of Akdeniz University.

JE9005486