886 *J. Chem. Eng. Data* **2006,** *51,* 886−891

Osmotic and Activity Coefficients of Short-Chain Alkyl Benzene Sulfonates by Vapor Pressure Osmometry

Vikrant B. Wagle and Vilas G. Gaikar*

Institute of Chemical Technology, University of Mumbai, Matunga, Mumbai 400 019, India

Osmotic coefficients ϕ for aqueous solutions of sodium salts of *n*-butyl benzene sulfonate (NaNBBS), isobutyl benzene sulfonate (NaIBBS), *tert*-butyl benzene sulfonate (NaTBBS), *n*-propyl benzene sulfonate (NaPBS), ethyl benzene sulfonate (NaEBS), and *p*-toluene sulfonate (NaPTS) have been determined as a function of their molality m at 40 °C, 45 °C, and 50 °C by vapor pressure osmometry. Plots of ϕ versus $1/m$ show breaks yielding minimum hydrotropic molality (MHM) of the six hydrotropes. Burchfield and Woolley's model of micelle formation of ionic surfactants gives an apt representation of the experimental data.

Introduction

Short-chain alkyl benzene sulfonate hydrotropes are highly water-soluble amphiphilic organic compounds similar to surfactants but with a shorter hydrophobic part. As a result, they show a milder surface activity and a characteristic minimum hydrotropic concentration (MHC), usually in a range of (0.1 to 0.8) mol·dm^{-3}, to reduce the surface tension of aqueous solutions to constant values.[1] There is a growing evidence toward the aggregation tendency of short-chain alkyl benzene sulfonates because of their surface active nature although at one time they were treated as electrolytes.[1,2] The extent and mechanism of the self-association of hydrotropes, however, are the subject of debate because of poor knowledge of the structures and properties of these solutions.[3] The newer applications of hydrotropes in chemical engineering/technology have spurred research into hydrotropy in the recent years. An understanding of the properties of hydrotropes either in the dispersed or aggregated states in aqueous solutions gains a practical importance.[4,5]

As a part of our ongoing study to understand the solution characteristics of hydrotropes, we have selected sodium salts of *n*-butyl benzene sulfonate (NaNBBS), isobutyl benzene sulfonate (NaIBBS), *tert*-butyl benzene sulfonate (NaTBBS), *n*-propyl benzene sulfonate (NaPBS), ethyl benzene sulfonate (NaEBS), and *p*-toluene sulfonate (NaPTS). The difference in the solution properties of these hydrotropes must originate from the difference in the structures of the alkyl group on the aromatic ring as the rest of the molecule remains the same. In this paper, the results of vapor pressure osmometry studies of aqueous solutions of the hydrotropes at 40 °C, 45 °C, and 50 °C are reported. In addition, the data were analyzed by using Burchfield and Woolley's model of ionic surfactant solutions.[6]

Experimental Section

Materials. *n*-Butyl benzene and isobutyl benzene were obtained from Herdillia Chemicals Ltd. (≈ 98 % purity) while *tert*-butyl benzene, *n*-propyl benzene, and ethyl benzene were obtained from Spectrochem (99 % purity). Purity of all hydrocarbons was verified by gas−liquid chromatography (GLC). The chromatograms obtained from GLC showed the presence of other hydrocarbons in a very small amount (< 1 %). The impurities were not individually identified. NaPTS was obtained from Navdeep Chemicals, Mumbai. The other sulfonates were prepared by sulfonation of the corresponding alkyl benzenes following a reported procedure for the aromatic sulfonates.[7] The impurities, such as inorganic salts, were removed from the hydrotropes by its repeated recrystallization from methanol. The recrystallized hydrotropes were dried at 60 °C for (15 to 18) h till a free-flowing powder was obtained. All the hydrotrope solutions were prepared using double-distilled deionized water.

Method. The vapor pressure osmometry measurements were carried out with a Knauer vapor pressure osmometer (model K-7000) at 40 °C, 45 °C, and 50 °C. The osmometer consists of two thermistors that are placed in an airtight cell. Experiments were conducted by placing a drop of a hydrotrope solution on one thermistor and a drop of water on the other. The two drops assume different temperatures, which in turn lead to a change in resistance of the two thermistors. This difference in the vapor pressures of the sample and solution droplets was measured in terms of ΔR, the difference in the resistances of the two thermistors. The osmometer was calibrated using NaCl solution as a standard,[8] and the calibration factor k was calculated as $(55.5 \pm 2) \times 10^{-5}\ \Omega^{-1}\cdot\text{mol}\cdot\text{kg}^{-1}$, $(52.25 \times 10^{-5})\ \Omega^{-1}\cdot\text{mol}\cdot\text{kg}^{-1}$ and $(49.0 \pm 1) \times 10^{-5}\ \Omega^{-1}\cdot\text{mol}\cdot\text{kg}^{-1}$ for 40 °C, 45 °C, and 50 °C, respectively. The osmotic coefficient ϕ of the hydrotrope solutions of molality m was then calculated with eq 1:[9]

$$\nu\phi m = k\Delta R \tag{1}$$

where ν is the number of ions into which an electrolyte dissociates, which in the case of sodium alkyl benzene sulfonates is 2.

The minimum hydrotropic molality (MHM) of the hydrotropes (expressed in mol·kg^{-1}) have been converted to MHC (in mol·dm^{-3}) using the densities of the hydrotrope solutions measured using an Anton Paar DMA-6000 density meter having a resolution of $\pm\ 10^{-6}$ g·cm^{-3}

---

* Corresponding author. Fax: +91-22-24145614. E-mail: v.g.gaikar@udct.org.

10.1021/je050348f CCC: $33.50

Table 1. Osmotic and Activity Coefficient Data of Sodium *p*-Toluene Sulfonate at 40 °C, 45 °C, and 50 °C

m	t = 40 °C		t = 45 °C		t = 50 °C		t = 25 °C[11]	
mol·kg^{-1}	ϕ	γ	ϕ	γ	ϕ	γ	m/mol·kg^{-1}	ϕ
0.02	0.985 ± 0.039	0.973 ± 0.066	0.980 ± 0.037	0.962 ± 0.044	0.968 ± 0.035	0.922 ± 0.036		
0.04	0.964 ± 0.011	0.937 ± 0.016	0.960 ± 0.018	0.924 ± 0.039	0.956 ± 0.010	0.887 ± 0.028		
0.06	0.944 ± 0.013	0.902 ± 0.010	0.941 ± 0.007	0.889 ± 0.023	0.939 ± 0.012	0.852 ± 0.013		
0.08	0.933 ± 0.010	0.876 ± 0.027	0.931 ± 0.009	0.863 ± 0.022	0.928 ± 0.005	0.829 ± 0.015		
0.10	0.921 ± 0.005	0.852 ± 0.014	0.920 ± 0.004	0.840 ± 0.025	0.916 ± 0.004	0.805 ± 0.017	0.10	0.924
0.12	0.911 ± 0.007	0.830 ± 0.010	0.908 ± 0.006	0.817 ± 0.026	0.904 ± 0.006	0.783 ± 0.019		
0.14	0.902 ± 0.006	0.811 ± 0.015	0.898 ± 0.003	0.797 ± 0.021	0.894 ± 0.003	0.763 ± 0.017		
0.15	0.897 ± 0.005	0.801 ± 0.015	0.895 ± 0.005	0.789 ± 0.019	0.892 ± 0.005	0.756 ± 0.019		
0.16	0.891 ± 0.003	0.791 ± 0.011	0.888 ± 0.005	0.778 ± 0.025	0.885 ± 0.003	0.745 ± 0.016		
0.17	0.888 ± 0.005	0.783 ± 0.009	0.887 ± 0.004	0.771 ± 0.019	0.882 ± 0.004	0.738 ± 0.018		
0.20	0.867 ± 0.004	0.744 ± 0.009	0.864 ± 0.002	0.731 ± 0.021	0.860 ± 0.003	0.698 ± 0.016	0.20	0.907
0.22	0.876 ± 0.004	0.759 ± 0.013	0.873 ± 0.002	0.746 ± 0.021	0.869 ± 0.003	0.713 ± 0.016		
0.30	0.839 ± 0.002	0.690 ± 0.009	0.836 ± 0.002	0.678 ± 0.022	0.831 ± 0.002	0.646 ± 0.012	0.30	0.897
0.35	0.806 ± 0.002	0.651 ± 0.010	0.803 ± 0.001	0.639 ± 0.018	0.800 ± 0.001	0.610 ± 0.014		
0.40	0.771 ± 0.001	0.612 ± 0.009	0.760 ± 0.002	0.594 ± 0.016	0.755 ± 0.002	0.563 ± 0.013	0.40	0.887
0.45	0.760 ± 0.002	0.588 ± 0.008	0.756 ± 0.001	0.575 ± 0.016	0.750 ± 0.002	0.546 ± 0.012		
0.50	0.750 ± 0.001	0.567 ± 0.008	0.743 ± 0.001	0.553 ± 0.016	0.739 ± 0.001	0.526 ± 0.011	0.50	0.880
0.60	0.720 ± 0.001	0.525 ± 0.008	0.711 ± 0.001	0.509 ± 0.014	0.696 ± 0.001	0.479 ± 0.010	0.60	0.874
0.70	0.710 ± 0.001	0.497 ± 0.007	0.685 ± 0.001	0.474 ± 0.013	0.676 ± 0.001	0.447 ± 0.009	0.70	0.867
0.80	0.701 ± 0.001	0.474 ± 0.007	0.683 ± 0.001	0.453 ± 0.013	0.674 ± 0.001	0.427 ± 0.008	0.80	0.861

Table 2. Osmotic and Activity Coefficient Data of Sodium Ethyl Benzene Sulfonate at 40 °C, 45 °C, and 50 °C

m	t = 40 °C		t = 45 °C		t = 50 °C	
mol·kg^{-1}	ϕ	γ	ϕ	γ	ϕ	γ
0.02	0.971 ± 0.039	0.933 ± 0.041	0.967 ± 0.037	0.920 ± 0.053	0.956 ± 0.035	0.884 ± 0.032
0.04	0.957 ± 0.020	0.898 ± 0.014	0.954 ± 0.018	0.884 ± 0.047	0.949 ± 0.017	0.851 ± 0.012
0.06	0.939 ± 0.011	0.863 ± 0.030	0.936 ± 0.012	0.849 ± 0.042	0.935 ± 0.007	0.820 ± 0.011
0.08	0.916 ± 0.008	0.826 ± 0.024	0.914 ± 0.005	0.814 ± 0.040	0.913 ± 0.009	0.784 ± 0.016
0.10	0.899 ± 0.008	0.796 ± 0.016	0.896 ± 0.007	0.782 ± 0.048	0.892 ± 0.007	0.752 ± 0.019
0.12	0.881 ± 0.004	0.767 ± 0.020	0.877 ± 0.006	0.752 ± 0.043	0.876 ± 0.003	0.724 ± 0.015
0.14	0.866 ± 0.006	0.741 ± 0.021	0.860 ± 0.003	0.725 ± 0.040	0.858 ± 0.005	0.701 ± 0.014
0.15	0.858 ± 0.003	0.728 ± 0.019	0.855 ± 0.005	0.714 ± 0.043	0.851 ± 0.003	0.685 ± 0.014
0.16	0.841 ± 0.005	0.709 ± 0.037	0.839 ± 0.003	0.697 ± 0.035	0.838 ± 0.004	0.669 ± 0.015
0.17	0.829 ± 0.005	0.693 ± 0.015	0.814 ± 0.004	0.672 ± 0.038	0.813 ± 0.005	0.646 ± 0.014
0.20	0.788 ± 0.004	0.645 ± 0.018	0.765 ± 0.002	0.615 ± 0.030	0.771 ± 0.003	0.599 ± 0.010
0.22	0.761 ± 0.002	0.614 ± 0.016	0.754 ± 0.003	0.597 ± 0.039	0.748 ± 0.002	0.572 ± 0.010
0.30	0.717 ± 0.003	0.527 ± 0.070	0.692 ± 0.001	0.514 ± 0.041	0.679 ± 0.002	0.489 ± 0.011
0.40	0.626 ± 0.002	0.451 ± 0.012	0.614 ± 0.002	0.431 ± 0.033	0.611 ± 0.001	0.412 ± 0.008
0.50	0.568 ± 0.001	0.389 ± 0.010	0.560 ± 0.001	0.373 ± 0.029	0.560 ± 0.001	0.357 ± 0.006
0.60	0.545 ± 0.001	0.351 ± 0.008	0.533 ± 0.001	0.334 ± 0.027	0.528 ± 0.001	0.318 ± 0.005
0.70	0.516 ± 0.001	0.317 ± 0.008	0.504 ± 0.001	0.301 ± 0.026	0.499 ± 0.001	0.286 ± 0.005
0.80	0.504 ± 0.001	0.293 ± 0.007	0.493 ± 0.001	0.278 ± 0.024	0.487 ± 0.001	0.265 ± 0.004

The standard uncertainty in the ΔR reading obtained from the instrument was ± 1 Ω, and the maximum variation was within ± 2 % of the measured value. The standard uncertainty in the molality of the hydrotrope solutions prepared was within ± 0.5 mmol·kg^{-1}.[10] The cell temperature, which is electronically controlled, has a standard uncertainty of $\pm 1 \times 10^{-3}$ °C. The expanded standard uncertainty in both the measured variables and the derived parameters (ϕ and $\gamma_\pm$) has been calculated by taking the coverage factor as 2, which corresponds to a level of confidence L near 95 %.[11] The combined standard uncertainty (i.e., the uncertainty derived by the propagation of uncertainty in composition, temperature, and ΔR into those for the osmotic and activity coefficients) is shown in Tables 1 to 6.

Results and Discussion

The mean molal activity coefficients and osmotic coefficients of the hydrotropes as a function of molality m at 40 °C, 45 °C, and 50 °C are given in Tables 1 to 6 with combined standard uncertainties in osmotic and activity coefficients. The osmotic coefficients of NaPTS are compared with those reported by Robinson and Stokes[12] using isopiestic vapor pressure measurements at 25 °C in Table 1. The present values reported at 40 °C, 45 °C, and 50 °C show a clear break near 0.35 mol·kg^{-1}, the literature values of Na−PTS show the break 0.5 mol·kg^{-1} at 25 °C. The osmotic coefficients of *p*-toluene sulfonate obtained by Robinson and Stokes[12] at 25 °C and those reported in this paper are comparable when the concentration of sodium toluene sulfonate in the aqueous solutions is in the dilute concentration range. However, the values differ only at higher hydrotrope concentrations. The unit is, however, not equipped to handle the measurements at 25 °C for direct comparison with the published data. However, the reported values of osmotic coefficients at 50 °C of a surfactant, sodium dodecyl sulfate, and those measured by the same Knauer vapor pressure osmometer unit are in close agreement with a maximum difference of 1.4 %.[13]

The osmotic coefficients ϕ of these hydrotropes were further used to calculate the mean molal activity coefficients $\gamma_\pm$ of the hydrotropes considering their strong ionic characteristics. The osmotic and activity coefficients are related to the molality m of the solution through the Gibbs−Duhem equation:[14]

$$\ln \gamma_\pm = \phi - 1 + \int_0^m (\phi - 1)\, \mathrm{d}(\ln m) \tag{2}$$

The activity of water a_w can be related to the osmotic coefficient ϕ of a hydrotrope by eq 3; G_2^{ni}, the nonideality contribution to

Table 3. Osmotic and Activity Coefficient Data of Sodium *n*-Propyl Benzene Sulfonate at 40 °C, 45 °C, and 50 °C

m	$t = 40$ °C		$t = 45$ °C		$t = 50$ °C	
mol·kg^{-1}	ϕ	γ	ϕ	γ	ϕ	γ
0.02	0.957 ± 0.039	0.894 ± 0.035	0.954 ± 0.037	0.878 ± 0.042	0.943 ± 0.035	0.844 ± 0.033
0.047	0.945 ± 0.017	0.846 ± 0.039	0.939 ± 0.016	0.828 ± 0.017	0.933 ± 0.015	0.793 ± 0.032
0.056	0.930 ± 0.014	0.825 ± 0.021	0.914 ± 0.013	0.798 ± 0.010	0.910 ± 0.007	0.763 ± 0.020
0.08	0.891 ± 0.010	0.769 ± 0.028	0.888 ± 0.005	0.749 ± 0.027	0.885 ± 0.009	0.718 ± 0.025
0.09	0.880 ± 0.005	0.750 ± 0.026	0.885 ± 0.008	0.737 ± 0.015	0.882 ± 0.004	0.705 ± 0.023
0.12	0.849 ± 0.007	0.699 ± 0.025	0.847 ± 0.004	0.683 ± 0.010	0.841 ± 0.006	0.652 ± 0.022
0.13	0.840 ± 0.005	0.685 ± 0.020	0.840 ± 0.006	0.670 ± 0.015	0.827 ± 0.005	0.634 ± 0.016
0.14	0.814 ± 0.006	0.659 ± 0.023	0.801 ± 0.003	0.636 ± 0.015	0.819 ± 0.005	0.621 ± 0.017
0.15	0.784 ± 0.005	0.631 ± 0.017	0.782 ± 0.005	0.615 ± 0.011	0.777 ± 0.005	0.586 ± 0.014
0.16	0.763 ± 0.003	0.608 ± 0.018	0.761 ± 0.003	0.594 ± 0.009	0.756 ± 0.003	0.566 ± 0.015
0.18	0.731 ± 0.004	0.572 ± 0.016	0.729 ± 0.004	0.557 ± 0.009	0.725 ± 0.004	0.531 ± 0.016
0.20	0.687 ± 0.002	0.531 ± 0.015	0.684 ± 0.002	0.518 ± 0.013	0.678 ± 0.002	0.492 ± 0.013
0.30	0.585 ± 0.003	0.412 ± 0.013	0.582 ± 0.002	0.412 ± 0.009	0.578 ± 0.001	0.383 ± 0.011
0.40	0.515 ± 0.002	0.339 ± 0.011	0.511 ± 0.001	0.329 ± 0.009	0.507 ± 0.002	0.313 ± 0.009
0.50	0.470 ± 0.001	0.289 ± 0.009	0.467 ± 0.001	0.281 ± 0.009	0.464 ± 0.001	0.267 ± 0.008
0.60	0.417 ± 0.001	0.248 ± 0.008	0.415 ± 0.002	0.241 ± 0.008	0.412 ± 0.001	0.229 ± 0.007
0.70	0.388 ± 0.001	0.220 ± 0.007	0.386 ± 0.001	0.214 ± 0.008	0.381 ± 0.001	0.202 ± 0.006
0.80	0.360 ± 0.001	0.197 ± 0.006	0.352 ± 0.001	0.190 ± 0.008	0.349 ± 0.001	0.182 ± 0.005

Table 4. Osmotic and Activity Coefficient Data of Sodium *n*-Butyl Benzene Sulfonate at 40 °C, 45 °C, and 50 °C

m	$t = 40$ °C		$t = 45$ °C		$t = 50$ °C	
mol·kg^{-1}	ϕ	γ	ϕ	γ	ϕ	γ
0.02	0.916 ± 0.039	0.811 ± 0.025	0.914 ± 0.021	0.789 ± 0.014	0.907 ± 0.035	0.766 ± 0.021
0.04	0.881 ± 0.011	0.731 ± 0.012	0.875 ± 0.018	0.708 ± 0.022	0.870 ± 0.010	0.686 ± 0.010
0.06	0.837 ± 0.008	0.662 ± 0.010	0.858 ± 0.007	0.658 ± 0.012	0.858 ± 0.012	0.640 ± 0.017
0.08	0.822 ± 0.010	0.619 ± 0.007	0.820 ± 0.009	0.607 ± 0.007	0.818 ± 0.005	0.589 ± 0.007
0.10	0.816 ± 0.005	0.590 ± 0.008	0.812 ± 0.004	0.572 ± 0.019	0.811 ± 0.004	0.559 ± 0.002
0.11	0.795 ± 0.004	0.568 ± 0.008	0.791 ± 0.007	0.556 ± 0.007	0.786 ± 0.006	0.538 ± 0.005
0.12	0.747 ± 0.007	0.531 ± 0.006	0.766 ± 0.006	0.532 ± 0.006	0.761 ± 0.005	0.515 ± 0.007
0.14	0.710 ± 0.003	0.490 ± 0.007	0.707 ± 0.003	0.482 ± 0.008	0.703 ± 0.003	0.466 ± 0.005
0.16	0.675 ± 0.005	0.455 ± 0.006	0.673 ± 0.005	0.447 ± 0.006	0.668 ± 0.002	0.432 ± 0.005
0.20	0.624 ± 0.004	0.399 ± 0.005	0.622 ± 0.002	0.392 ± 0.006	0.619 ± 0.003	0.379 ± 0.005
0.30	0.506 ± 0.002	0.298 ± 0.004	0.503 ± 0.002	0.292 ± 0.004	0.500 ± 0.001	0.282 ± 0.003
0.40	0.413 ± 0.002	0.232 ± 0.003	0.410 ± 0.002	0.228 ± 0.004	0.408 ± 0.002	0.220 ± 0.002
0.50	0.359 ± 0.001	0.192 ± 0.002	0.356 ± 0.001	0.188 ± 0.002	0.353 ± 0.001	0.182 ± 0.000
0.60	0.310 ± 0.001	0.162 ± 0.002	0.308 ± 0.001	0.159 ± 0.002	0.305 ± 0.001	0.153 ± 0.002
0.70	0.285 ± 0.001	0.142 ± 0.004	0.283 ± 0.001	0.139 ± 0.003	0.278 ± 0.001	0.133 ± 0.002
0.80	0.265 ± 0.000	0.126 ± 0.001	0.263 ± 0.000	0.123 ± 0.001	0.256 ± 0.000	0.118 ± 0.001

Table 5. Osmotic and Activity Coefficient Data of Sodium Isobutyl Benzene Sulfonate at 40 °C, 45 °C, and 50 °C

m	$t = 40$ °C		$t = 45$ °C		$t = 50$ °C	
mol·kg^{-1}	ϕ	γ	ϕ	γ	ϕ	γ
0.02	0.930 ± 0.039	0.811 ± 0.037	0.927 ± 0.037	0.806 ± 0.025	0.919 ± 0.035	0.784 ± 0.028
0.04	0.923 ± 0.020	0.766 ± 0.019	0.921 ± 0.018	0.760 ± 0.024	0.913 ± 0.017	0.736 ± 0.010
0.06	0.911 ± 0.008	0.732 ± 0.014	0.910 ± 0.012	0.726 ± 0.022	0.907 ± 0.012	0.705 ± 0.018
0.08	0.895 ± 0.010	0.701 ± 0.022	0.892 ± 0.009	0.693 ± 0.013	0.888 ± 0.005	0.673 ± 0.017
0.10	0.888 ± 0.005	0.679 ± 0.016	0.886 ± 0.007	0.672 ± 0.017	0.884 ± 0.007	0.653 ± 0.012
0.12	0.879 ± 0.004	0.659 ± 0.018	0.877 ± 0.004	0.653 ± 0.014	0.878 ± 0.003	0.635 ± 0.012
0.14	0.821 ± 0.006	0.607 ± 0.013	0.817 ± 0.005	0.600 ± 0.016	0.816 ± 0.008	0.583 ± 0.012
0.16	0.784 ± 0.003	0.570 ± 0.013	0.782 ± 0.005	0.564 ± 0.015	0.779 ± 0.003	0.547 ± 0.010
0.20	0.726 ± 0.004	0.510 ± 0.014	0.724 ± 0.004	0.503 ± 0.013	0.720 ± 0.003	0.488 ± 0.011
0.30	0.594 ± 0.002	0.389 ± 0.010	0.591 ± 0.001	0.384 ± 0.009	0.588 ± 0.001	0.372 ± 0.008
0.40	0.490 ± 0.002	0.308 ± 0.008	0.487 ± 0.002	0.303 ± 0.006	0.484 ± 0.002	0.293 ± 0.006
0.50	0.410 ± 0.001	0.251 ± 0.007	0.408 ± 0.001	0.248 ± 0.006	0.406 ± 0.001	0.239 ± 0.005
0.60	0.372 ± 0.001	0.216 ± 0.006	0.370 ± 0.001	0.213 ± 0.005	0.366 ± 0.001	0.206 ± 0.005
0.70	0.347 ± 0.001	0.191 ± 0.005	0.345 ± 0.001	0.188 ± 0.004	0.342 ± 0.002	0.182 ± 0.004
0.80	0.310 ± 0.001	0.168 ± 0.004	0.308 ± 0.001	0.166 ± 0.003	0.306 ± 0.002	0.160 ± 0.004

the chemical potential of a hydrotrope, is given by eq 4 if it is considered as a strong electrolyte:

$$\ln a_{\mathrm{w}} = -\frac{\nu m M_1}{1000}\phi \tag{3}$$

$$G_2^{\mathrm{ni}} = \nu RT \ln \gamma_{\pm} \tag{4}$$

where ν is the number of ions into which a hydrotrope dissociates and M_1 is the molecular weight of the solvent.

The aromatic sulfonates were earlier assumed to form stacked aggregates in aqueous solutions.[1] The change in activity of water is a very good indication of the onset of aggregation as the number of free particles decreases once the aggregation sets in. Figure 1 shows very small but noticeable break in activity of water a_{w} as a function of concentration for all the six hydrotropes at 40 °C. Figure 2 represents the change in G_2^{ni} as a function of concentration for all the hydrotropes at 40 °C. Similar changes are observed in a_{w} and G_2^{ni} at other two temperatures. The change in G_2^{ni} is attributable to the formation of the aggregates in the solutions. Since the headgroups of hydrotrope molecules are strongly ionic, their aggregation number should be limited.

Table 6. Osmotic and Activity Coefficient Data of Sodium *tert*-Butyl Benzene Sulfonate at 40 °C, 45 °C, and 50 °C

m	$t = 40$ °C		$t = 45$ °C		$t = 50$ °C	
mol·kg^{-1}	ϕ	γ	ϕ	γ	ϕ	γ
0.02	0.957 ± 0.039	0.892 ± 0.042	0.954 ± 0.037	0.880 ± 0.033	0.943 ± 0.035	0.864 ± 0.047
0.04	0.950 ± 0.020	0.857 ± 0.038	0.947 ± 0.018	0.845 ± 0.036	0.943 ± 0.010	0.829 ± 0.026
0.06	0.934 ± 0.008	0.823 ± 0.021	0.932 ± 0.012	0.815 ± 0.030	0.927 ± 0.012	0.797 ± 0.025
0.08	0.926 ± 0.010	0.801 ± 0.027	0.924 ± 0.005	0.789 ± 0.029	0.919 ± 0.005	0.771 ± 0.018
0.10	0.919 ± 0.009	0.781 ± 0.018	0.917 ± 0.007	0.770 ± 0.027	0.914 ± 0.007	0.755 ± 0.019
0.12	0.911 ± 0.007	0.764 ± 0.025	0.908 ± 0.004	0.751 ± 0.028	0.904 ± 0.003	0.733 ± 0.021
0.14	0.902 ± 0.006	0.746 ± 0.024	0.898 ± 0.002	0.732 ± 0.025	0.896 ± 0.003	0.718 ± 0.021
0.16	0.891 ± 0.006	0.728 ± 0.024	0.888 ± 0.005	0.715 ± 0.024	0.885 ± 0.004	0.698 ± 0.016
0.20	0.792 ± 0.004	0.639 ± 0.016	0.789 ± 0.002	0.629 ± 0.022	0.786 ± 0.003	0.612 ± 0.012
0.30	0.614 ± 0.002	0.472 ± 0.015	0.612 ± 0.002	0.463 ± 0.016	0.609 ± 0.001	0.452 ± 0.012
0.40	0.562 ± 0.002	0.400 ± 0.014	0.559 ± 0.002	0.414 ± 0.030	0.558 ± 0.002	0.381 ± 0.008

The association of hydrotrope molecules in the aqueous solutions is revealed more by the osmotic properties of the solutions. Figures 3 and 4 show variation in the activity and osmotic coefficients of the hydrotropes as a function of 1/m at 40 °C, respectively. Both ϕ and $\gamma_{\pm}$ give sharp breaks at the respective MHM values of the hydrotropes. The MHM values from these breaks for the hydrotropes are reported in Table 7. The reported MHC values of the hydrotropes obtained by surface tension[1,15] and dye solubilization measurements[16] are nearly similar to those reported in this paper. The variation in slopes of these curves indicate solute−solute interactions on self-aggregation of hydrotrope molecules and aggregate−aggregate interaction with increasing hydrotrope concentration.

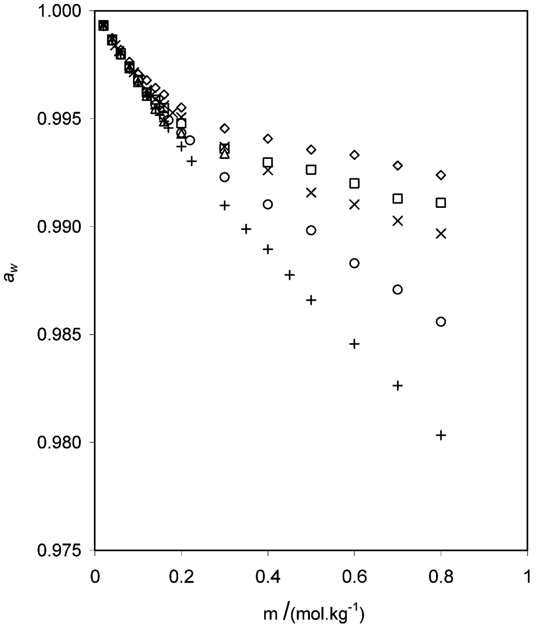

Figure 1. Activity of water at 40 °C in aqueous solution of ◇, NaNBBS; □, NaIBBS; △, NaTBBS; ×, NaPBS; ○, NaEBS; +, NaPTS.

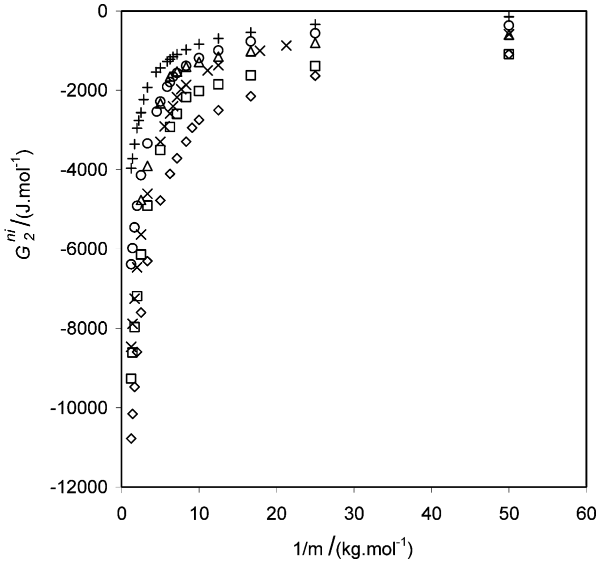

Figure 2. Nonideal free energy G_2^{ni} at 40 °C of aqueous solution of ◇, NaNBBS; □, NaIBBS; △, NaTBBS; ×, NaPBS; ○, NaEBS; +, NaPTS.

Burchfield and Woolley[6] extended the Guggenheim equation of mixed electrolytes to the solutions of surfactants using a mass-action treatment involving a single surfactant aggregate species, with the assumption that the surfactant is a strong 1:1 electrolyte at infinite dilution. The aggregate structure in this model is considered as a partially dissociated polyelectrolyte. The treatment can be applied in the same manner to the aggregates of the hydrotropes.

The final expression for the molal osmotic coefficient is given in eq 5:

$$(1-\phi) = \frac{\alpha(1+\beta-1/n)}{2} + \frac{\ln(10)A_{\gamma}I^{3/2}\sigma(bI^{1/2})}{3m} - B_{1\gamma}\left[\frac{(1-\alpha)(1-\beta\alpha)m(\ln 10)}{2}\right] - B_{n\gamma}\left[\frac{\alpha(1-\beta\alpha)m(\ln 10)}{2n}\right] \quad (5)$$

where A_{γ} is the Debye−Huckel parameter for activity coefficients (0.5221, 0.5291, and 0.5342 for water at 40 °C, 45 °C, and 50 °C, respectively[6]); m is the molality of the hydrotrope

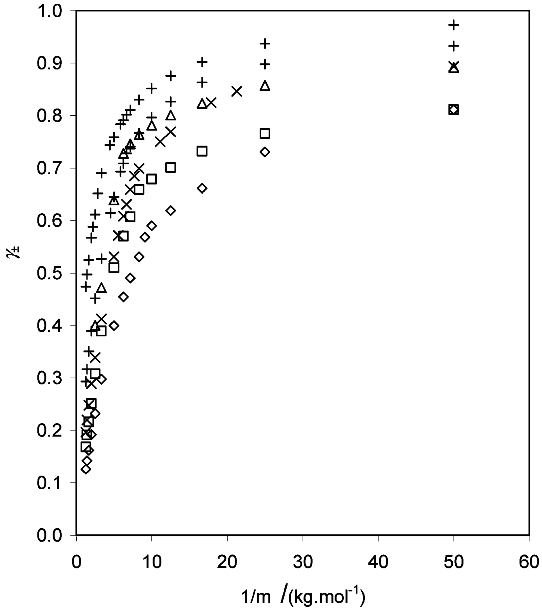

Figure 3. Activity coefficient γ of ◇, NaNBBS; □, NaIBBS; △, NaTBBS; ×, NaPBS; ○, NaEBS; +, NaPTS.

Table 7. Minimum Hydrotropic Molality *m*, Minimum Hydrotropic Concentration *c*, Density *ρ*, and Burchfield−Woolley Model Parameters $B_{1\gamma}$ and $B_{n\gamma}$ for Hydrotropes at 40 °C, 45 °C, and 50 °C

		MHM	MHC			$t = 40$ °C		$t = 45$ °C		$t = 50$ °C	
	density ρ	m mol·kg^{-1}	c mol·dm^{-3}	surface tension[1,15]	dye solubilization[16]	$B_{1\gamma}$ kg·mol^{-1}	$B_{n\gamma}$ kg·mol^{-1}	$B_{1\gamma}$ kg·mol^{-1}	$B_{n\gamma}$ kg·mol^{-1}	$B_{1\gamma}$ kg·mol^{-1}	$B_{n\gamma}$ kg·mol^{-1}
NaNBBS	1.003861	0.10	0.098	0.10	0.10	−0.63	30.16	−0.61	30.19	−0.64	30.32
NaIBBS	1.005113	0.12	0.117	0.12		−0.42	29.13	−0.53	29.5	−0.65	29.76
NaTBBS	1.007532	0.16	0.155	0.17	0.20	−0.35	25.78	−0.37	25.98	−0.41	26.55
NaPBS	1.005925	0.13	0.127	0.13	0.12	−0.36	17.94	−0.38	18.06	−0.40	18.34
NaEBS	1.008401	0.16	0.156	0.16	0.18	−0.21	10.46	−0.22	11.58	−0.25	10.42
NaPTS	1.022075	0.35	0.336	0.35	0.40	−0.18	10.09	−0.18	10.18	−0.19	10.26

solution; I is the ionic strength of the solution; b is an ion-size parameter ($b = 1.0$);[6] and $B_{1\gamma}$ and $B_{n\gamma}$ are Guggenheim parameters for counterion−monomer and counterion−aggregate interactions, respectively,

The ionic strength is determined from eq 6 where δ is a screening factor introduced to reduce the charge on the aggregate:

$$I = \frac{[2(1-\alpha) + n\delta^2(1-\beta)^2\alpha + (1-\beta)\alpha]m}{2} \qquad (6)$$

The function $\sigma(y)$ is determined by eq 7:

$$\sigma(y) = \frac{3[1 + y - 1/(1+y) - 2\ln(1+y)]}{y^3} \qquad (7)$$

Due to the structural similarity of the alkyl benzene sulfonates with that of a surfactant, we analyzed the osmotic coefficient data of hydrotrope solutions using the Burchfield−Woolley model.[6] Hydrotropes, too, behave as strong 1:1 electrolytes at infinite dilution. This model was tested with respect to the experimental data by taking $n = 2$ to $n = 50$ for each of the hydrotropes. The model gave the best fit for the osmotic coefficient data when the aggregation number (n) for NaBBS isomers, NaPBS, NaEBS, and NaPTS were taken as 35, 28, 22, and 18, respectively. The aggregation number estimated for NaNBBS by this model is closer to that obtained by the small angle neutron scattering (SANS) experiments.[17]

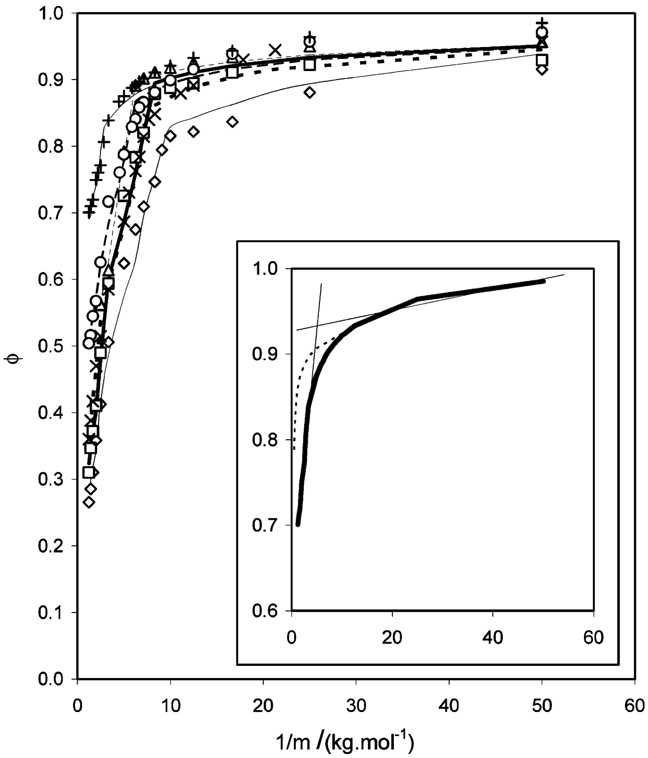

Figure 4. Osmotic coefficient ϕ of ◇, NaNBBS; □, NaIBBS; △, NaTBBS; ×, NaPBS; ○, NaEBS; +, NaPTS. The inset figure gives data for NaPTS (dotted line), Robinson et al.;[11] (solid line), this work. Intersection of the two extrapolated lines indicates the MHC of NaPTS.

The Burchfield−Woolley model treatment could not, however, adequately represent the concentration dependence of osmotic coefficients with a single value of δ, for all the hydrotropes. Since that counterion binding is likely to increase with the total hydrotrope and hydrotrope aggregate concentrations, δ was varied in the range of 0.2 to 0.75 for the best fit over the entire range of concentration. This indicates partial association of the counterions with the hydrotrope aggregates which increases with the increase in hydrotrope concentration. Figure 4 also shows the osmotic coefficients predicted from the Burchfield−Woolley model.

The reported analysis of the osmotic coefficient of sodium dodecyl sulfate and octylamine hydrobromide at temperatures ranging from 5 °C to 45 °C,had revealed insignificant interaction parameters $B_{1\gamma}$ and $B_{n\gamma}$ for both cationic and anionic surfactants.[6] Unlike the surfactant solutions, $B_{1\gamma}$ and $B_{n\gamma}$ are significant for all six hydrotropes. The values of $B_{1\gamma}$ and $B_{n\gamma}$ estimated for NaNBBS, NaIBBS, NaTBBS, NaPBS, NaEBS, and NaPTS are given in Table 7. NaNBBS shows a comparatively a greater extent of counterion binding and increased counterion−monomer and counterion−aggregate interactions as reflected in $B_{1\gamma}$ and $B_{n\gamma}$ values, which decrease in the order of NaNBBS, NaPBS, NaEBS, and NaPTS. These results indicate a strong interaction not only between hydrotrope monomer and its counterion, but because of a significant charge on the hydrotrope aggregates, between the hydrotrope aggregates and the counterions. Because of the highly charged nature of the aggregates, interaction between the aggregates cannot be ruled out.

Conclusion

Osmotic coefficients for aqueous solutions of NaNBBS, NaIBBS, NaTBBS, NaPBS, NaEBS, and NaPTS determined as a function of hydrotrope concentration show the aggregating tendency of the hydrotropes with increasing number of aggregates with the hydrotrope concentration. Plot of ϕ versus m showed well-defined breaks that correspond to the MHC of these hydrotropes. The Burchfield−Woolley model for aggregation of surfactants describes activity and osmotic coefficient data for all the hydrotropes over a wide range of concentration to yield the corresponding specific ion−interaction parameters.

Literature Cited

(1) Balasubramanian, D.; Shrinivas, V.; Gaikar V. G.; Sharma M. M. Aggregation behavior of hydrotrope compounds in aqueous solution. *J. Phys. Chem.* **1989**, *93*, 3865−3870.

(2) McKee, R. H. Use of hydrotrope solution in industries. *Ind. Eng. Chem. Ind. Ed.* **1946**, *38*, 382−385.

(3) Srinivas, V.; Rodley A.; Ravikumar K.; Robinson W. T.; Turnbull M. M.; Balasubramanian D. Molecular organization in hydrotropic assemblies. *Langmuir* **1997**, *13*, 3235−3239.

(4) Dandekar, D. V., Gaikar, V. G. Hydrotropic extraction of curcuminoids from turmeric. *Sep. Sci. Technol*. **2003**, *38* (5), 1185−1215.

(5) Raman, G., Gaikar V. G. Extraction of piperine from piper nigrum by hydrotropic solubilization. *Ind. Eng. Chem. Res*. **2002**, *41*, 2966−2976.

(6) Burchfield, T. E.; Woolley, E. M. Model for thermodynamics of ionic surfactant solutions. 1. Osmotic and activity coefficients. *J. Phys. Chem.* **1984**, *88*, 2149−2155.

(7) Furniss, B. S.; Hannaford, A. J.; Roger, S. V., Smith, P. W. G.; Tatchell, A. R. *Vogel's Textbook of Practical Organic Chemistry*, 4th ed.; John Wiley and Sons: New York, 1978; p 640.

(8) Gibbard, H. F.; Scatchard, D.; Rousseau, R.; Creek, J. L. Liquid−vapor equilibrium of aqueous sodium chloride, from 298 to 373K and from 1 to 6 $\text{mol}\cdot\text{kg}^{-1}$, and related properties. *J. Chem. Eng. Data* **1974**, *19*, 281−288.

(9) Robinson, R. A.; Stokes, R. H. *Electrolyte Solutions*, 2nd ed.; Buttersworths: London, 1959.

(10) Thomas, W. V. *Quantifying Measurement Uncertainty in Analytical Chemistry—A Simplified Practical Approach*; NIST: Gaithersburg, MD.

(11) Chirico, R. D.; Frenkel, M.; Diky, V. V.; Marsh, K. N. Wilhoit, R. C. ThermoML—an XML based approach for storage and exchange of experimental and critically evaluated thermophysical and thermochemical property data. 2.Uncertainties. *J. Chem. Eng. Data.* **2003**, *48*, 1344−1369.

(12) Robinson R. A.; Stokes R. H. Tables of osmotic and activity coefficients of electrolytes in aqueous solutions at 25 °C. *Trans. Faraday Soc.* **1949**, *45*, 612−624.

(13) Rajagopalan, N.; Vadnere, M.; Lindenbaum, S. Thermodynamics of aqueous bile salt solutions: heat capacity, enthalpy and entropy of dilution. *J. Solution Chem.* **1981**, *10*, 785.

(14) Desnoyers, J. E.; Perron G.; Roux A. H. *Surfactant Solutions*: *New Method of Investigation*; Zana, R., Ed.; Dekker: New York/Basel, 1987; Vol. 1, Chapter 1.

(15) Bhat, M.; Gaikar, V. G. Characterization of interaction between butyl benzene sulfonates and cetyl pyridinium chloride in mixed aggregate systems. *Langmuir* **1999**, *15,* 4740−4751.

(16) Pal, O. R. Ph.D. Dissertation, University of Mumbai, December 2003.

(17) Pal, O. R.; Gaikar, V. G.; Joshi, J. V.; Goyal, P. S.; Aswal, V. K.; Seth, E. Small angle neutron scattering studies of sodium butyl benzene sulfonate aggregates in aqueous solution. *Pramana—J. Phys.* **2004**, *63* (2), 357−362.

Received for review August 26, 2005. Accepted March 17, 2006.

JE050348F