# Vapor Pressure Osmometry and Conductivity Studies of Aqueous Solutions of Sodium Alkyl Glycol Sulfates and Sodium Alkyl Carbitol Sulfates as Hydrotropes

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The temperature dependence of the degree of ionization and standard free energy of aggregation of aqueous solutions of sodium alkyl glycol sulfates and sodium alkyl carbitol sulfates, viz., sodium methyl monoethylene glycol sulfate (NaMMGS), sodium ethyl monoethylene glycol sulfate (NaEMGS), sodium propyl monoethylene glycol sulfate (NaPMGS), sodium butyl monoethylene glycol sulfate (NaBMGS), sodium methyl diethylene glycol(carbitol) sulfate (NaMDGS), and sodium butyl diethylene glycol sulfate (NaBDGS), have been determined from conductivity data in the temperature range of (40 to 50) °C. The osmotic coefficients $\phi$ and activity coefficients of sodium alkyl monoethylene glycol sulfates and sodium alkyl carbitol sulfates determined by vapor pressure osmometry at molalities ranging from (0.02 to 1.8) $\text{mol}\cdot\text{kg}^{-1}$ show their aggregating tendency which decreases with temperature. The minimum hydrotropic concentrations from the plots of specific conductivity $\kappa$ vs $m$ and plots of $\phi$ vs $m$ match well for all the hydrotropes. The osmotic coefficient data for each hydrotrope when treated with the Burchfield and Woolley model show strong aggregate−counterion association and yield an aggregation number in the range 8 to 17.

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## Introduction

Hydrotropes are highly water-soluble organic salts and increase solubility of other water-insoluble organic compounds in their aqueous solutions. Alkaline metal salts of alkyl glycol sulfates and alkyl carbitol sulfates form one set of such hydrotropic compounds. Their amphiphilic molecular structure leads to a mild surface activity when dissolved in water. Analogous to the critical micellar concentration of a surfactant, hydrotropes show a characteristic minimum hydrotrope concentration (MHC), depending on their structures, beyond which they are presumed to form aggregates in solutions.[1,2] The formation of such aggregates is considered a prerequisite for the hydrotropic effect, and knowledge of the MHC becomes important in various applications.[3] Sodium butyl monoglycol sulfate, the most typical of the alkyl glycol and alkyl carbitol sulfate based hydrotropes, is widely used in the preparation of cleaning emulsions and bleaching solutions.[1,3]

Balasubramanian et al.[3] were the first to report the MHC of 0.8 $\text{mol}\cdot\text{dm}^{-3}$ for sodium butyl monoglycol sulfate. In this paper, we have used vapor pressure osmometry to understand the solution properties of these hydrotropes in aqueous solutions as well as specific conductivity data to determine the degree of ionization and standard free energy of aggregation of aqueous hydrotrope solutions. We have selected sodium *n*-butyl monoethylene glycol sulfate (NaBMGS), sodium *n*-propyl monoethylene glycol sulfate (NaPMGS), sodium ethyl monoethylene glycol sulfate (NaEMGS), sodium methyl monoethylene glycol sulfate (NaMMGS), sodium methyl diethylene glycol sulfate (NaMDGS), and sodium *n*-butyl diethylene glycol sulfate (NaBDGS) as the hydrotropes. These hydrotropes were first reported by Sadwilkar et al.[1] for their efficiency in dissolving water-insoluble organic compounds to conduct organic condensation reactions in aqueous solutions. The hydrophobic structure of the hydrotrope was shown to have an effect on hydrotropic solubilization as well as on reaction rates in such a medium. In recent years, Bauduin et al.[5] have compared short chain alkyl mono- and dipropylene glycol ethers as cosolvents with hydrotropes. These nonionic propylene glycol ethers, because of the absence of any ionic group, are similar in behavior to water miscible cosolvents including glycols. However, these authors also indicated a significant effect of the hydrophobicity of the alkyl group on the solubilization capacity of their aqueous solutions.

The systematic study of solution properties, such as activity and osmotic coefficients, as a function of hydrotrope structure and temperature allows one to correlate the hydrotrope behavior in solution with its structure. Sodium alkyl glycol and alkyl carbitol sulfates provide an interesting case in which the presence of an additional ethoxide group in the carbitol structure shows an effect on the solution properties of these hydrotropes. Also, the difference in the solution properties of sodium alkyl glycol sulfates must originate from the structure of the alkyl group attached to the ethylene oxide group of the hydrotrope. Taking into account the need to study the temperature dependence of these properties, in this paper, we report our results of conductivity and vapor pressure osmometry measurements of the aqueous solutions of sodium alkyl monoethylene glycol and carbitol sulfates at three different temperatures. The osmotic coefficient data were further analyzed by Burchfield and Woolley's model[4] of ionic surfactant solutions to obtain various parameters and aggregation numbers of the hydrotrope aggregates.

## Experimental Section

2-Methoxy ethanol [109-86-4] (99.5 % purity), 2-ethoxyethanol [110-80-5] (98.5 % purity), chlorosulfonic acid [7790-94-5] (98 % purity), 2-butoxyethanol [111-76-2] (98 % purity), methyldigol [111-77-3] (97 % purity), butyldigol [112-34-5] (97 % purity), hydrochloric acid [7647-01-0] (35.4 % purity), and sodium hydroxide [1310-73-2] (purity 98 %) were obtained from

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SD Fine Chemicals. Ltd., while 2-propoxyethanol was obtained from Fluka having 99 % purity. All the chemicals were used as received.

The sulfation of the glycols and carbitols was carried out in a fully baffled cylindrical glass reactor equipped with a six-blade impellor and placed in a constant temperature bath. Arrangements were made for the dropwise addition of chlorosulfonic acid to the alkoxyethanol placed in the reactor. A slight vacuum was applied to remove the HCl fumes liberated during the reaction. The rate of addition of chlorosulfonic acid was regulated to control the temperature of the reaction under vigorously agitating conditions. The acid was then neutralized to its sodium salt by addition of std. NaOH solution. The salt was then lyophilized to yield flaky crystals of the hydrotrope. The hydrotropes were then purified by repeated crystallization from ethanol to remove the inorganic salts and then dried under vacuum for 10 h. All the hydrotrope solutions were prepared using doubly distilled deionized water.

## Method

***Vapor Pressure Osmometry.*** The vapor pressure osmometry measurements were carried out with a Knauer vapor pressure osmometer (model K-7000), at three different temperatures, 40 °C, 45 °C, and 50 °C. The details of the unit and relevant procedure for estimation of osmotic coefficients are reported in our previous paper on osmotic and activity coefficients of alkyl benzene sulfonate hydrotropes.[6] The minimum hydrotropic molality (MHM) of the hydrotropes expressed in $\text{mol}\cdot\text{kg}^{-1}$ have been converted to minimum hydrotropic concentration (MHC) in $\text{mol}\cdot\text{dm}^{-3}$ using the densities of the hydrotrope solutions measured using an Anton Paar DMA-6000 density meter having a uncertainty of $\pm\ 10^{-6}\ \text{g}\cdot\text{cm}^{-3}$.

The standard uncertainty in the difference between the two thermistor readings of the osmometer was ± 1 ohm, and the maximum difference was within ± 2 % of the measured value. The standard uncertainty in the molality of the hydrotrope solutions prepared was within $\pm\ 0.5\ \text{mmol}\cdot\text{kg}^{-1}$.[7] The osmometer cell temperature was electronically controlled with a standard uncertainty of $\pm\ 1\cdot10^{-3}$ °C. The expanded standard uncertainty in both the measured variables and the derived parameters, $\phi$ and $\gamma_{\pm}$, has been calculated by taking the coverage factor as 2 which corresponds to a level of confidence $L$ near 95 %.[8] There are no data of physicochemical properties of aqueous solutions of alkyl glycol sulfates or alkyl carbitol sulfates, available in the literature for comparison, but the osmometer was characterized in our earlier studies for alkyl benzene sulfonate hydrotropes and gave a maximum difference of 1.5 % from the reported values of osmotic coefficient of surfactants and one of the hydrotropes.[6]

## Results and Discussion

***Conductivity Studies.*** The specific conductivity of aqueous solutions of the sulfates was measured at different concentrations at 40 °C, 45 °C, and 50 °C. The results of specific conductivity measurements for the six hydrotropes at 40 °C are shown in Figure 1. At the other two temperatures, the behavior is similar. The increase in conductivity of hydrotropic solutions with concentration is expected to throw light on their minimum hydrotropic concentrations as well as on their nature of aggregation as the aggregation affects the number of free ions in solution. Above the MHC, the conductivity of the hydrotrope solution is not only due to the presence of free hydrotrope ions and counterions but also due to the charged aggregate species. Two linear segments in the conductivity versus molality plots can be seen, and the MHC of the hydrotrope was taken as the intersection of the apparently straight lines. The MHCs of the six hydrotropes are listed in Table 1. Assuming that the equivalent conductivity of the ionized hydrotrope in the aggregates is comparable to that of the free, unaggregated hydrotrope, the degree of ionization, α, of the aggregates was estimated from the ratio of slopes of the linear segments above and below the MHC.[9]

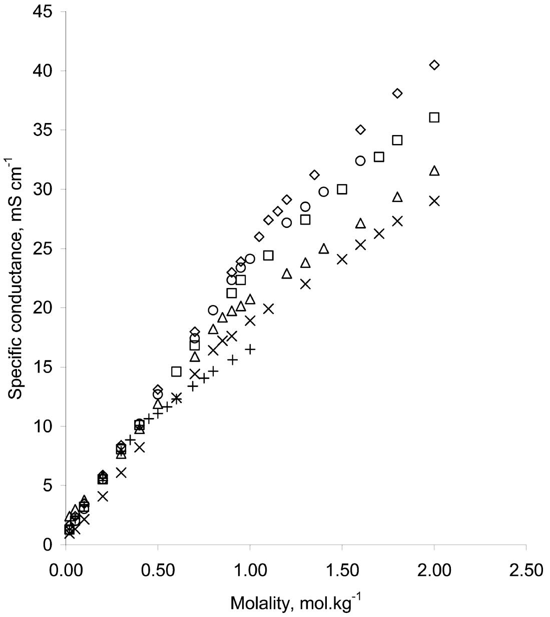

**Figure 1.** Specific conductivity of alkyl monoethylene glycol and carbitol sulfates as a function of concentration at 40 °C. ◇, NaMMGS; □, NaEMGS; △, NaPMGS; ×, NaBMGS; ○, NaMDGS; +, NaBDGS.

The degree of counterion binding, $\beta$, and standard free energy of aggregation, $\Delta G^{\text{o}}_{\text{agg}}$, which is related to α have been calculated by using the following equations

$$\beta_{\text{cb}} = 1 - \alpha \tag{1}$$

$$\Delta G^{\text{o}}_{\text{agg}} = (2 - \alpha)RT \ln X_{\text{MHC}} \tag{2}$$

where $X_{\text{MHC}}$ is the value of MHC expressed in mole fraction.[10]

The temperature-dependent values of α, $\beta_{\text{cb}}$, and $\Delta G^{\text{o}}_{\text{agg}}$ are also reported in Table 1. The degree of ionization, α, increases with an increase in temperature. Higher values of α with temperature clearly indicate increased ionization of the aggregates with increasing temperature. The standard free energies of aggregation calculated for the six hydrotropes decrease with temperature. The low rate of decrease of $\Delta G^{\text{o}}_{\text{agg}}$ with increasing temperature results from an entropy−enthalpy compensation effect.[11−13] Comparing the magnitudes of $\Delta G^{\text{o}}_{\text{agg}}$ of the six sulfates clearly suggests that the aggregation formation is energetically as well as entropically more favorable in NaBDGS than the other hydrotropes. However, these values are much lower when compared to surfactants such as decyldimethylbenzylammonium chloride ($28.0\ \text{kJ}\cdot\text{mol}^{-1}$)[14] and tetradecyl- ($39.1\ \text{kJ}\cdot\text{mol}^{-1}$) and hexadecyldimethylbenzylammonium chlorides ($43.9\ \text{kJ}\cdot\text{mol}^{-1}$)[15]

From the conductivity data, the MHCs of the hydrotropes were also obtained by using a local polynomial regression method (LPRM) to establish a relationship between conductivity and concentration.[16] The method was applied by performing weighted local fittings of polynomial functions by least-squares.

**Table 1. MHC ($\text{mol}\cdot\text{kg}^{-1}$), Degree of Ionization ($\alpha$), Degree of Counterion Binding ($\beta_{\text{cb}}$), and Free Energy of Aggregation ($\Delta G^{\text{o}}_{\text{agg}}/\text{kJ}\cdot\text{mol}^{-1}$) of Alkyl Monoethylene Glycol and Carbitol Sulfates at 40 °C, 45 °C, and 50 °C**

| hydrotrope | MHC | $\alpha_{40}$ | $\alpha_{45}$ | $\alpha_{50}$ | $\beta_{\text{cb},40}$ | $\beta_{\text{cb},45}$ | $\beta_{\text{cb},50}$ | $\Delta G^{\text{o}}_{40}$ | $\Delta G^{\text{o}}_{45}$ | $\Delta G^{\text{o}}_{50}$ |
|---|---|---|---|---|---|---|---|---|---|---|
| NaBMGS | 0.80 | 0.525 | 0.531 | 0.549 | 0.475 | 0.469 | 0.451 | −16.33 | −16.53 | −16.58 |
| NaPMGS | 0.85 | 0.530 | 0.548 | 0.550 | 0.470 | 0.452 | 0.450 | −16.04 | −16.10 | −16.34 |
| NaEMGS | 0.95 | 0.590 | 0.607 | 0.629 | 0.410 | 0.393 | 0.371 | −14.99 | −15.04 | −15.04 |
| NaMMGS | 1.10 | 0.616 | 0.621 | 0.635 | 0.384 | 0.379 | 0.365 | −14.19 | −14.36 | −14.44 |
| NaBDGS | 0.40 | 0.480 | 0.491 | 0.528 | 0.520 | 0.509 | 0.472 | −18.66 | −18.82 | −18.65 |
| NaMDGS | 0.95 | 0.583 | 0.609 | 0.617 | 0.417 | 0.391 | 0.383 | −15.06 | −15.02 | −15.17 |

**Table 2. MHC Obtained by the Graphical and LPRM Method of Alkyl Monoethylene Glycol and Carbitol Sulfates at 40 °C, 45 °C, and 50 °C**

| | graphical method | LPRM method | | |
|---|---|---|---|---|
| | $\text{MHC}_{40}$ | $\text{MHC}_{40}$ | $\text{MHC}_{45}$ | $\text{MHC}_{50}$ |
| hydrotrope | $\text{mol}\cdot\text{kg}^{-1}$ | $\text{mol}\cdot\text{kg}^{-1}$ | $\text{mol}\cdot\text{kg}^{-1}$ | $\text{mol}\cdot\text{kg}^{-1}$ |
| NaBMGS | 0.80 | 0.80 | 0.76 | 0.73 |
| NaPMGS | 0.85 | 0.88 | 0.81 | 0.87 |
| NaEMGS | 0.95 | 0.92 | 0.91 | 0.97 |
| NaMMGS | 1.10 | 1.10 | 1.10 | 1.11 |
| NaBDGS | 0.40 | 0.38 | 0.39 | 0.37 |
| NaMDGS | 0.95 | 0.96 | 0.98 | 0.96 |

In the present case, a regression function using a polynomial of odd order is necessary, at least of a third order, to compute the MHC by Philip's definition (eq 3).[17]

$$\left(\frac{d^3\kappa}{dC_T^3}\right)_{C_T=\text{CMC}} = 0 \tag{3}$$

where $\kappa$ denotes the conductivity and $C_T$ is the hydrotrope's total concentration in the solution.

The derivatives of the regression curve were estimated by the local polynomial regression estimators in MATLAB, using the quartic kernel and plug-in optimal asymptotic mean squared error (AMSE) bandwidth.[18] The ideal optimal bandwidth in the fitting process was estimated from the variance of the errors, $\sigma^2$, using a local polynomial regression with a pilot bandwidth. The Parzen−Rosenblatt kernel estimator[19] for $f(C_T)$ was obtained by using a pilot bandwidth and a parametric regression. The reason for using a local bandwidth, and therefore applying AMSE criteria to obtain the bandwidth parameter, is that the objective we are after is not as much to have an overall view of the regression function but more to locate the point that proves a particular MHC.

Table 2 shows the MHC values obtained by the regression analysis of the conductivity data for all the hydrotropes at 40 °C, 45 °C, and 50 °C. In general, a good concordance exists between the MHC values obtained by both the graphical and the LPRM methods.

***Vapor Pressure Osmometry.*** The method of estimation of osmotic coefficients and activity coefficients from osmometry measurements of electrolyte solutions has been described in detail in previous reports.[6,20] The estimated osmotic coefficients of the hydrotropes as a function of molality ($m$, $\text{mol}\cdot\text{kg}^{-1}$) at 40 °C, 45 °C, and 50 °C are given in Table 3 with uncertainties in each value.

The osmotic coefficients ($\phi$) 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.[20]

$$\ln \gamma_\pm = \phi - 1 + \int_0^m (\phi - 1)\mathrm{d}(\ln m) \tag{4}$$

The osmotic coefficients ($\phi$) of the hydrotropes were further used to calculate the mean molal activity coefficients ($\gamma_\pm$) of the hydrotropes considering their strong ionic characteristics which are also reported in Table 3. The standard deviation in the osmotic and activity coefficients of the hydrotropes have been calculated from repeated measurements and was within ± 2 % of the measured values.

The activity of water ($a_\text{w}$) can be related to the osmotic coefficient ($\phi$) of a hydrotrope by eq 5, and the nonideality contribution to the chemical potential of a hydrotrope is given by eq 6 if it is considered as a strong electrolyte dissociating completely in the aqueous solutions.[20]

$$\ln a_\text{w} = -\frac{\nu m M_1}{1000}\phi \tag{5}$$

$$G_2^{ni} = \nu RT \ln \gamma_\pm \tag{6}$$

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

Figure 2 shows the change in activity of water ($a_\text{w}$) as a function of concentration for all six hydrotropes at 40 °C. At two other temperatures, the behavior of the hydrotrope solution is similar. 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. The greater the extent of aggregation among hydrotrope molecules, the lesser will be the number of free hydrotrope molecules in the aqueous solution. By virtue of better aggregation of NaBDGS in aqueous solutions and decrease in total number of charged aggregates, the activity of water in the case of NaBDGS solutions is slightly greater when compared to that in the presence of other hydrotropes. The decrease in the activity of water in the presence of alkyl glycol and alkyl carbitol sulfates is also more than that observed in alkyl benzene sulfonates, indicating higher aggregation number in the latter case. Figure 3 shows the change in $G_2^{ni}$ as a function of hydrotrope concentration for all the hydrotropes at 40 °C. Similar changes are observed in ($a_\text{w}$) and $G_2^{ni}$ at the other two temperatures for all the hydrotropes. The overall negative values of $G_2^{ni}$ suggest a compatibility between the hydrotropes and water, probably because of the glycol chains present in the hydrotrope structures. An appreciable change in $G_2^{ni}$ after the MHCs is attributable to the formation of the aggregates in the solutions. However, these values are lower in magnitude than those previously reported for nonyl- and decyltrimethylammonium bromide (NTABr and DTABr) surfactants.[21] At 45 °C, for NTABr and DTABr, reported $G_2^{ni}$ values at 0.5 $\text{mol}\cdot\text{kg}^{-1}$ were (−8715 and −11115) $\text{J}\cdot\text{mol}^{-1}$, respectively, while the $G_2^{ni}$ values obtained for the hydrotropes at 0.5 $\text{mol}\cdot\text{kg}^{-1}$ are in the range of (600 to 2500) $\text{J}\cdot\text{mol}^{-1}$. Much higher values, in the same range as the surfactants, were observed in the case of short chain alkyl benzene sulfonate hydrotropes.[6] The alkyl glycol and alkyl carbitol sulfates carry

**Table 3. Osmotic and Activity Coefficient Data at 40 °C, 45°C, and 50°C**

| *m* | 40 °C | | 45 °C | | 50 °C | |
|---|---|---|---|---|---|---|
| mol·kg$^{-1}$ | $\phi$ | $\gamma$ | $\phi$ | $\gamma$ | $\phi$ | $\gamma$ |
| Hydrotrope: Na−Methyl Monoethylene Glycol Sulfate | | | | | | |
| 0.02 | 0.993 ± 0.0055 | 0.985 ± 0.0062 | 0.992 ± 0.0131 | 0.982 ± 0.0142 | 0.992 ± 0.0061 | 0.980 ± 0.0049 |
| 0.05 | 0.987 ± 0.0056 | 0.971 ± 0.0013 | 0.982 ± 0.0052 | 0.962 ± 0.0206 | 0.980 ± 0.0049 | 0.958 ± 0.0009 |
| 0.10 | 0.985 ± 0.0028 | 0.960 ± 0.0108 | 0.979 ± 0.0000 | 0.948 ± 0.0160 | 0.977 ± 0.0024 | 0.944 ± 0.0091 |
| 0.20 | 0.975 ± 0.0000 | 0.938 ± 0.0052 | 0.971 ± 0.0013 | 0.924 ± 0.0175 | 0.967 ± 0.0000 | 0.919 ± 0.0090 |
| 0.30 | 0.970 ± 0.0009 | 0.923 ± 0.0056 | 0.966 ± 0.0009 | 0.908 ± 0.0173 | 0.961 ± 0.0008 | 0.903 ± 0.0111 |
| 0.50 | 0.950 ± 0.0000 | 0.888 ± 0.0054 | 0.949 ± 0.0005 | 0.875 ± 0.0155 | 0.947 ± 0.0005 | 0.872 ± 0.0069 |
| 0.70 | 0.939 ± 0.0004 | 0.862 ± 0.0049 | 0.936 ± 0.0004 | 0.848 ± 0.0150 | 0.932 ± 0.0000 | 0.840 ± 0.0107 |
| 0.90 | 0.930 ± 0.0006 | 0.841 ± 0.0045 | 0.927 ± 0.0006 | 0.825 ± 0.0154 | 0.925 ± 0.0003 | 0.818 ± 0.0092 |
| 0.95 | 0.920 ± 0.0003 | 0.829 ± 0.0052 | 0.917 ± 0.0008 | 0.813 ± 0.0140 | 0.915 ± 0.0000 | 0.806 ± 0.0090 |
| 1.05 | 0.905 ± 0.0000 | 0.809 ± 0.0048 | 0.901 ± 0.0010 | 0.793 ± 0.0151 | 0.896 ± 0.0014 | 0.784 ± 0.0079 |
| 1.10 | 0.895 ± 0.0008 | 0.797 ± 0.0041 | 0.891 ± 0.0002 | 0.782 ± 0.0143 | 0.887 ± 0.0000 | 0.773 ± 0.0091 |
| 1.15 | 0.874 ± 0.0000 | 0.777 ± 0.0046 | 0.871 ± 0.0007 | 0.762 ± 0.0132 | 0.868 ± 0.0000 | 0.754 ± 0.0091 |
| 1.20 | 0.856 ± 0.0002 | 0.758 ± 0.0047 | 0.853 ± 0.0007 | 0.744 ± 0.0129 | 0.849 ± 0.0002 | 0.736 ± 0.0086 |
| 1.37 | 0.825 ± 0.0002 | 0.720 ± 0.0044 | 0.821 ± 0.0000 | 0.705 ± 0.0126 | 0.819 ± 0.0002 | 0.697 ± 0.0071 |
| 1.60 | 0.800 ± 0.0003 | 0.682 ± 0.0043 | 0.779 ± 0.0002 | 0.655 ± 0.0119 | 0.783 ± 0.0003 | 0.651 ± 0.0055 |
| 1.80 | 0.785 ± 0.0003 | 0.655 ± 0.0038 | 0.781 ± 0.0003 | 0.639 ± 0.0117 | 0.778 ± 0.0005 | 0.631 ± 0.0047 |
| Hydrotrope: Na−Ethyl Monoethylene Glycol Sulfate | | | | | | |
| 0.02 | 0.985 ± 0.0083 | 0.956 ± 0.0063 | 0.982 ± 0.0026 | 0.946 ± 0.0030 | 0.980 ± 0.0122 | 0.942 ± 0.0132 |
| 0.05 | 0.987 ± 0.0055 | 0.947 ± 0.0016 | 0.982 ± 0.0052 | 0.931 ± 0.0038 | 0.975 ± 0.0049 | 0.919 ± 0.0064 |
| 0.10 | 0.979 ± 0.0028 | 0.926 ± 0.0002 | 0.977 ± 0.0000 | 0.914 ± 0.0007 | 0.975 ± 0.0024 | 0.902 ± 0.0297 |
| 0.20 | 0.975 ± 0.0000 | 0.910 ± 0.0030 | 0.970 ± 0.0000 | 0.891 ± 0.0001 | 0.967 ± 0.0000 | 0.879 ± 0.0115 |
| 0.30 | 0.967 ± 0.0009 | 0.892 ± 0.0021 | 0.963 ± 0.0009 | 0.873 ± 0.0007 | 0.960 ± 0.0008 | 0.860 ± 0.0112 |
| 0.40 | 0.949 ± 0.0014 | 0.867 ± 0.0038 | 0.945 ± 0.0007 | 0.847 ± 0.0010 | 0.940 ± 0.0006 | 0.833 ± 0.0111 |
| 0.60 | 0.936 ± 0.0005 | 0.839 ± 0.0045 | 0.931 ± 0.0004 | 0.814 ± 0.0030 | 0.927 ± 0.0000 | 0.798 ± 0.0135 |
| 0.70 | 0.921 ± 0.0000 | 0.815 ± 0.0028 | 0.916 ± 0.0000 | 0.794 ± 0.0007 | 0.913 ± 0.0004 | 0.780 ± 0.0103 |
| 0.90 | 0.896 ± 0.0003 | 0.777 ± 0.0021 | 0.893 ± 0.0003 | 0.757 ± 0.0002 | 0.891 ± 0.0000 | 0.742 ± 0.0112 |
| 0.95 | 0.890 ± 0.0003 | 0.768 ± 0.0027 | 0.887 ± 0.0003 | 0.749 ± 0.0007 | 0.883 ± 0.0003 | 0.735 ± 0.0096 |
| 1.00 | 0.871 ± 0.0000 | 0.749 ± 0.0030 | 0.867 ± 0.0000 | 0.729 ± 0.0018 | 0.863 ± 0.0000 | 0.713 ± 0.0114 |
| 1.05 | 0.851 ± 0.0003 | 0.729 ± 0.0022 | 0.847 ± 0.0002 | 0.710 ± 0.0007 | 0.845 ± 0.0005 | 0.697 ± 0.0093 |
| 1.10 | 0.830 ± 0.0000 | 0.709 ± 0.0023 | 0.827 ± 0.0005 | 0.690 ± 0.0021 | 0.825 ± 0.0002 | 0.676 ± 0.0110 |
| 1.30 | 0.788 ± 0.0002 | 0.658 ± 0.0020 | 0.785 ± 0.0000 | 0.641 ± 0.0005 | 0.780 ± 0.0004 | 0.627 ± 0.0083 |
| 1.50 | 0.763 ± 0.0000 | 0.621 ± 0.0020 | 0.760 ± 0.0002 | 0.604 ± 0.0016 | 0.757 ± 0.0002 | 0.591 ± 0.0095 |
| 1.70 | 0.745 ± 0.0002 | 0.592 ± 0.0018 | 0.741 ± 0.0003 | 0.576 ± 0.0007 | 0.738 ± 0.0001 | 0.564 ± 0.0073 |
| 1.80 | 0.739 ± 0.0002 | 0.579 ± 0.0018 | 0.737 ± 0.0001 | 0.564 ± 0.0015 | 0.734 ± 0.0001 | 0.552 ± 0.0090 |
| Hydrotrope: Na−Propyl Monoethylene Glycol Sulfate | | | | | | |
| 0.02 | 0.982 ± 0.0028 | 0.950 ± 0.0052 | 0.979 ± 0.0118 | 0.942 ± 0.0229 | 0.977 ± 0.0025 | 0.939 ± 0.0028 |
| 0.05 | 0.976 ± 0.0055 | 0.928 ± 0.0097 | 0.977 ± 0.0052 | 0.921 ± 0.0184 | 0.975 ± 0.0049 | 0.916 ± 0.0036 |
| 0.10 | 0.974 ± 0.0028 | 0.910 ± 0.0072 | 0.971 ± 0.0000 | 0.900 ± 0.0163 | 0.972 ± 0.0024 | 0.897 ± 0.0042 |
| 0.20 | 0.972 ± 0.0000 | 0.892 ± 0.0078 | 0.969 ± 0.0013 | 0.879 ± 0.0154 | 0.966 ± 0.0025 | 0.874 ± 0.0048 |
| 0.30 | 0.960 ± 0.0000 | 0.871 ± 0.0057 | 0.956 ± 0.0009 | 0.855 ± 0.0151 | 0.941 ± 0.0000 | 0.845 ± 0.0113 |
| 0.40 | 0.942 ± 0.0007 | 0.842 ± 0.0080 | 0.939 ± 0.0000 | 0.828 ± 0.0139 | 0.934 ± 0.0006 | 0.816 ± 0.0022 |
| 0.50 | 0.935 ± 0.0006 | 0.825 ± 0.0078 | 0.933 ± 0.0010 | 0.812 ± 0.0264 | 0.930 ± 0.0000 | 0.800 ± 0.0025 |
| 0.70 | 0.905 ± 0.0000 | 0.780 ± 0.0071 | 0.898 ± 0.0000 | 0.763 ± 0.0124 | 0.911 ± 0.0000 | 0.764 ± 0.0025 |
| 0.80 | 0.883 ± 0.0003 | 0.753 ± 0.0072 | 0.886 ± 0.0003 | 0.743 ± 0.0126 | 0.897 ± 0.0003 | 0.745 ± 0.0023 |
| 0.85 | 0.870 ± 0.0000 | 0.737 ± 0.0067 | 0.868 ± 0.0000 | 0.724 ± 0.0119 | 0.880 ± 0.0000 | 0.727 ± 0.0024 |
| 0.90 | 0.855 ± 0.0003 | 0.721 ± 0.0068 | 0.851 ± 0.0006 | 0.707 ± 0.0120 | 0.847 ± 0.0000 | 0.698 ± 0.0023 |
| 1.00 | 0.828 ± 0.0003 | 0.690 ± 0.0065 | 0.824 ± 0.0000 | 0.676 ± 0.0111 | 0.811 ± 0.0007 | 0.662 ± 0.0017 |
| 1.20 | 0.780 ± 0.0002 | 0.634 ± 0.0059 | 0.777 ± 0.0004 | 0.622 ± 0.0099 | 0.775 ± 0.0004 | 0.614 ± 0.0024 |
| 1.30 | 0.756 ± 0.0000 | 0.608 ± 0.0056 | 0.754 ± 0.0002 | 0.597 ± 0.0099 | 0.751 ± 0.0000 | 0.589 ± 0.0020 |
| 1.40 | 0.736 ± 0.0002 | 0.585 ± 0.0056 | 0.731 ± 0.0004 | 0.572 ± 0.0092 | 0.727 ± 0.0004 | 0.563 ± 0.0021 |
| 1.60 | 0.724 ± 0.0002 | 0.557 ± 0.0053 | 0.719 ± 0.0002 | 0.545 ± 0.0088 | 0.715 ± 0.0002 | 0.536 ± 0.0017 |
| 1.80 | 0.710 ± 0.0003 | 0.551 ± 0.0142 | 0.707 ± 0.0001 | 0.527 ± 0.0018 | 0.701 ± 0.0001 | 0.511 ± 0.0012 |
| Hydrotrope: Na−Butyl Monoethylene Glycol Sulfate | | | | | | |
| 0.02 | 0.985 ± 0.0042 | 0.957 ± 0.0032 | 0.979 ± 0.0131 | 0.944 ± 0.0416 | 0.978 ± 0.0110 | 0.942 ± 0.0102 |
| 0.05 | 0.976 ± 0.0028 | 0.933 ± 0.0007 | 0.975 ± 0.0019 | 0.921 ± 0.0156 | 0.970 ± 0.0049 | 0.913 ± 0.0050 |
| 0.10 | 0.974 ± 0.0000 | 0.916 ± 0.0033 | 0.971 ± 0.0026 | 0.900 ± 0.0118 | 0.967 ± 0.0000 | 0.893 ± 0.0091 |
| 0.20 | 0.958 ± 0.0014 | 0.882 ± 0.0041 | 0.956 ± 0.0026 | 0.866 ± 0.0084 | 0.953 ± 0.0012 | 0.856 ± 0.0092 |
| 0.30 | 0.944 ± 0.0009 | 0.852 ± 0.0032 | 0.940 ± 0.0000 | 0.835 ± 0.0096 | 0.937 ± 0.0000 | 0.824 ± 0.0082 |
| 0.40 | 0.926 ± 0.0000 | 0.822 ± 0.0024 | 0.922 ± 0.0007 | 0.805 ± 0.0102 | 0.918 ± 0.0006 | 0.793 ± 0.0072 |
| 0.60 | 0.901 ± 0.0005 | 0.774 ± 0.0022 | 0.896 ± 0.0000 | 0.756 ± 0.0096 | 0.893 ± 0.0004 | 0.740 ± 0.0009 |
| 0.70 | 0.890 ± 0.0000 | 0.754 ± 0.0021 | 0.887 ± 0.0004 | 0.737 ± 0.0087 | 0.885 ± 0.0000 | 0.725 ± 0.0068 |
| 0.80 | 0.854 ± 0.0003 | 0.714 ± 0.0018 | 0.850 ± 0.0000 | 0.697 ± 0.0085 | 0.847 ± 0.0003 | 0.686 ± 0.0062 |
| 0.90 | 0.822 ± 0.0000 | 0.679 ± 0.0018 | 0.818 ± 0.0003 | 0.662 ± 0.0082 | 0.814 ± 0.0000 | 0.651 ± 0.0061 |
| 1.00 | 0.780 ± 0.0003 | 0.638 ± 0.0015 | 0.778 ± 0.0000 | 0.623 ± 0.0076 | 0.776 ± 0.0002 | 0.613 ± 0.0056 |
| 1.10 | 0.739 ± 0.0005 | 0.598 ± 0.0013 | 0.737 ± 0.0002 | 0.584 ± 0.0073 | 0.734 ± 0.0000 | 0.574 ± 0.0054 |
| 1.30 | 0.685 ± 0.0002 | 0.540 ± 0.0013 | 0.683 ± 0.0004 | 0.527 ± 0.0063 | 0.680 ± 0.0002 | 0.517 ± 0.0049 |
| 1.50 | 0.666 ± 0.0004 | 0.505 ± 0.0011 | 0.663 ± 0.0000 | 0.493 ± 0.0060 | 0.660 ± 0.0002 | 0.484 ± 0.0044 |
| 1.70 | 0.650 ± 0.0002 | 0.476 ± 0.0012 | 0.647 ± 0.0002 | 0.464 ± 0.0055 | 0.643 ± 0.0000 | 0.455 ± 0.0043 |
| 1.80 | 0.647 ± 0.0002 | 0.479 ± 0.0147 | 0.645 ± 0.0001 | 0.460 ± 0.0001 | 0.641 ± 0.0001 | 0.446 ± 0.0041 |
| Hydrotrope: Na−Methyl Diethylene Glycol Sulfate | | | | | | |
| 0.02 | 0.984 ± 0.0139 | 0.953 ± 0.0014 | 0.981 ± 0.0015 | 0.945 ± 0.0010 | 0.977 ± 0.0101 | 0.939 ± 0.0095 |
| 0.05 | 0.982 ± 0.0055 | 0.937 ± 0.0079 | 0.980 ± 0.0022 | 0.927 ± 0.0191 | 0.975 ± 0.0049 | 0.917 ± 0.0045 |
| 0.10 | 0.975 ± 0.0028 | 0.919 ± 0.0079 | 0.971 ± 0.0026 | 0.906 ± 0.0018 | 0.967 ± 0.0024 | 0.893 ± 0.0022 |
| 0.20 | 0.972 ± 0.0000 | 0.898 ± 0.0104 | 0.970 ± 0.0000 | 0.884 ± 0.0026 | 0.967 ± 0.0012 | 0.872 ± 0.0011 |
| 0.30 | 0.961 ± 0.0009 | 0.877 ± 0.0114 | 0.958 ± 0.0009 | 0.862 ± 0.0034 | 0.954 ± 0.0000 | 0.849 ± 0.0000 |
| 0.40 | 0.944 ± 0.0000 | 0.851 ± 0.0098 | 0.941 ± 0.0000 | 0.836 ± 0.0028 | 0.940 ± 0.0006 | 0.822 ± 0.0005 |

**Table 3 Continued**

| $m$ | 40 °C | | 45 °C | | 50 °C | |
|---|---|---|---|---|---|---|
| mol·kg$^{-1}$ | $\phi$ | $\gamma$ | $\phi$ | $\gamma$ | $\phi$ | $\gamma$ |
| 0.50 | 0.929 ± 0.0011 | 0.826 ± 0.0090 | 0.924 ± 0.0005 | 0.809 ± 0.0022 | 0.921 ± 0.0000 | 0.797 ± 0.0000 |
| 0.70 | 0.909 ± 0.0000 | 0.788 ± 0.0091 | 0.907 ± 0.0000 | 0.773 ± 0.0024 | 0.905 ± 0.0004 | 0.759 ± 0.0003 |
| 0.80 | 0.886 ± 0.0003 | 0.760 ± 0.0084 | 0.883 ± 0.0003 | 0.743 ± 0.0015 | 0.880 ± 0.0000 | 0.732 ± 0.0000 |
| 0.90 | 0.880 ± 0.0000 | 0.744 ± 0.0085 | 0.876 ± 0.0003 | 0.734 ± 0.0020 | 0.871 ± 0.0003 | 0.713 ± 0.0002 |
| 0.95 | 0.870 ± 0.0003 | 0.732 ± 0.0085 | 0.867 ± 0.0003 | 0.722 ± 0.0020 | 0.862 ± 0.0005 | 0.704 ± 0.0004 |
| 1.00 | 0.847 ± 0.0000 | 0.711 ± 0.0081 | 0.845 ± 0.0000 | 0.696 ± 0.0021 | 0.841 ± 0.0002 | 0.682 ± 0.0221 |
| 1.20 | 0.801 ± 0.0002 | 0.657 ± 0.0108 | 0.799 ± 0.0002 | 0.645 ± 0.0067 | 0.796 ± 0.0004 | 0.632 ± 0.0003 |
| 1.30 | 0.771 ± 0.0004 | 0.627 ± 0.0075 | 0.766 ± 0.0004 | 0.613 ± 0.0021 | 0.763 ± 0.0004 | 0.600 ± 0.0002 |
| 1.40 | 0.760 ± 0.0000 | 0.609 ± 0.0070 | 0.764 ± 0.0002 | 0.599 ± 0.0002 | 0.748 ± 0.0000 | 0.582 ± 0.0000 |
| 1.60 | 0.751 ± 0.0002 | 0.585 ± 0.0068 | 0.748 ± 0.0007 | 0.572 ± 0.0013 | 0.745 ± 0.0002 | 0.559 ± 0.0001 |
| Hydrotrope: Na−Butyl Diethylene Glycol Sulfate | | | | | | |
| 0.02 | 0.971 ± 0.0139 | 0.919 ± 0.0152 | 0.966 ± 0.0000 | 0.911 ± 0.0008 | 0.967 ± 0.0000 | 0.900 ± 0.0020 |
| 0.05 | 0.960 ± 0.0055 | 0.882 ± 0.0068 | 0.956 ± 0.0052 | 0.871 ± 0.0061 | 0.955 ± 0.0049 | 0.863 ± 0.0016 |
| 0.10 | 0.946 ± 0.0000 | 0.842 ± 0.0101 | 0.943 ± 0.0026 | 0.830 ± 0.0062 | 0.940 ± 0.0024 | 0.821 ± 0.0021 |
| 0.20 | 0.919 ± 0.0014 | 0.784 ± 0.0108 | 0.915 ± 0.0013 | 0.770 ± 0.0029 | 0.911 ± 0.0012 | 0.758 ± 0.0014 |
| 0.30 | 0.898 ± 0.0009 | 0.740 ± 0.0099 | 0.896 ± 0.0000 | 0.724 ± 0.0064 | 0.893 ± 0.0011 | 0.715 ± 0.0014 |
| 0.40 | 0.885 ± 0.0007 | 0.708 ± 0.0087 | 0.882 ± 0.0007 | 0.695 ± 0.0039 | 0.880 ± 0.0003 | 0.683 ± 0.0009 |
| 0.45 | 0.876 ± 0.0000 | 0.691 ± 0.0088 | 0.872 ± 0.0006 | 0.678 ± 0.0030 | 0.867 ± 0.0006 | 0.665 ± 0.0005 |
| 0.50 | 0.869 ± 0.0006 | 0.677 ± 0.0091 | 0.864 ± 0.0000 | 0.663 ± 0.0032 | 0.861 ± 0.0000 | 0.652 ± 0.0008 |
| 0.55 | 0.849 ± 0.0000 | 0.655 ± 0.0085 | 0.846 ± 0.0005 | 0.642 ± 0.0036 | 0.843 ± 0.0003 | 0.631 ± 0.0011 |
| 0.60 | 0.826 ± 0.0005 | 0.631 ± 0.0085 | 0.789 ± 0.0004 | 0.594 ± 0.0032 | 0.786 ± 0.0006 | 0.583 ± 0.0010 |
| 0.69 | 0.797 ± 0.0004 | 0.597 ± 0.0080 | 0.793 ± 0.0004 | 0.583 ± 0.0034 | 0.790 ± 0.0000 | 0.573 ± 0.0057 |
| 0.75 | 0.769 ± 0.0004 | 0.571 ± 0.0077 | 0.764 ± 0.0003 | 0.557 ± 0.0026 | 0.761 ± 0.0004 | 0.546 ± 0.0005 |
| 0.80 | 0.758 ± 0.0000 | 0.556 ± 0.0073 | 0.756 ± 0.0000 | 0.544 ± 0.0027 | 0.751 ± 0.0008 | 0.532 ± 0.0009 |
| 0.90 | 0.730 ± 0.0003 | 0.524 ± 0.0067 | 0.727 ± 0.0003 | 0.512 ± 0.0027 | 0.724 ± 0.0000 | 0.503 ± 0.0007 |
| 1.00 | 0.706 ± 0.0003 | 0.497 ± 0.0066 | 0.703 ± 0.0003 | 0.486 ± 0.0026 | 0.700 ± 0.0004 | 0.476 ± 0.0008 |

much smaller hydrophobic groups, and the nonideal contribution seems to come from the hydrophobic structures.

The association of molecules in the aqueous solutions is revealed more by the osmotic properties of the hydrotrope solutions. Figure 4 shows the variation in activity coefficients of the hydrotropes as a function of molality ($m$) at 40 °C, while Figure 5 shows the osmotic coefficients of the hydrotropes as a function of $m$ at 40 °C. Both $\phi$ and $\gamma_\pm$ show an abrupt change near the respective MHCs of the hydrotropes. The MHCs from these breaks are also reported in Table 4 for the hydrotropes for comparison with MHCs obtained from other methods. The change in slopes of these curves with hydrotrope concentration indicates changes in solute−solute interactions on aggregation and in aggregate−aggregate interaction on increasing the hydrotrope concentration.

Burchfield and Woolley[4] extended the Guggenheim equation of mixed electrolytes to 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 has been applied in the same manner to the aggregates of the hydrotropes.[6] The basic relationships that summarize the model are given in eq 7 to eq 9

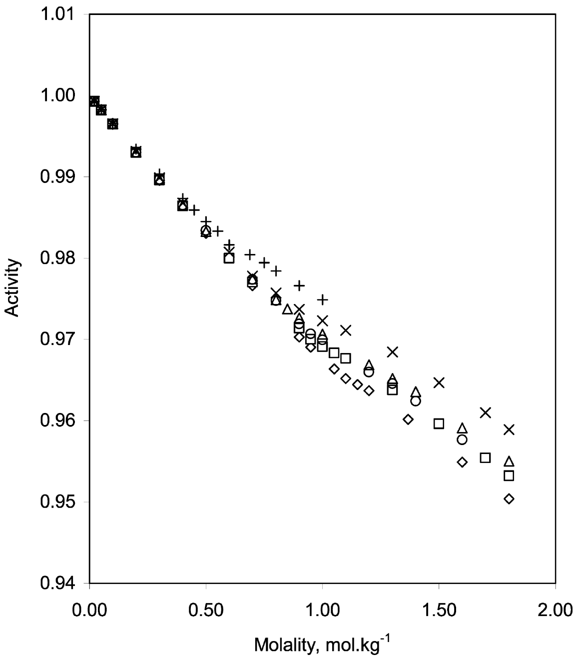

**Figure 2.** Activity of the water as a function of hydrotrope concentration at 40 °C. ◇, NaMMGS; □, NaEMGS; Δ, NaPMGS; ×, NaBMGS; ○, NaMDGS; +, NaBDGS.

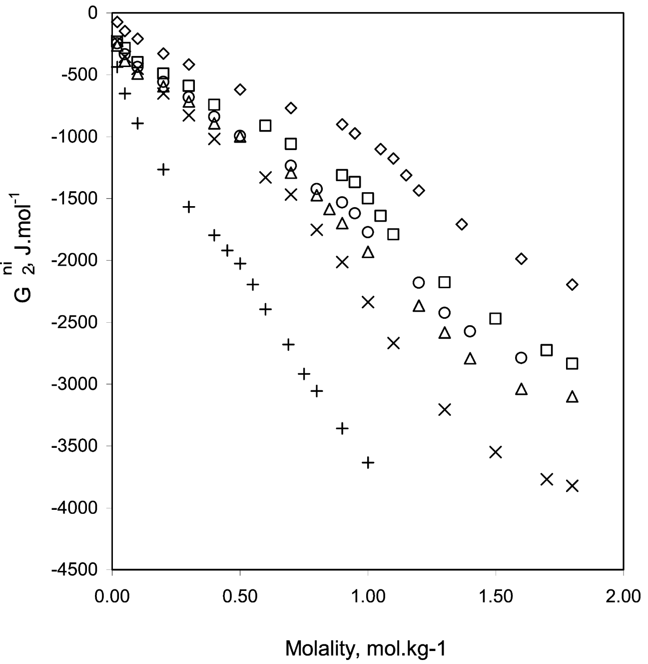

**Figure 3.** $G_2^{ni}$ as a function of hydrotrope concentration at 40 °C: ◇, NaMMGS; □, NaEMGS; Δ, NaPMGS; ×, NaBMGS; ○, NaMDGS; +, NaBDGS.

$$n\beta \mathrm{Na}^+ + n\mathrm{R{-}CH_2} - 3\mathrm{CH_2} - \mathrm{O} - \mathrm{SO_3^-} \leftrightarrow (\mathrm{Na}^+)_{n\beta}(\mathrm{RSO_3})_n^{-n(1-\beta)} \quad (7)$$

$$\log(\gamma_\pm) = \frac{-A_\gamma I^{1/2}}{(1 + bI^{1/2})} + \left(\frac{1}{2}\right)\log(1 - \alpha) + \left(\frac{1}{2}\right)\log(1 - \beta\alpha) + \frac{B_{1\gamma} m(2 - \alpha - \beta\alpha)}{2} + B_{n\gamma}(m\alpha/2n) \quad (8)$$

$$(1 - \phi) = \frac{\alpha(1 + \beta - 1/n)}{2} + \frac{\ln(10) A_\gamma I^{3/2} \sigma(bI^{1/2})}{3m} - B_{1\gamma}\left[\frac{(1 - \alpha)(1 - \beta\alpha)m(\ln 10)}{2}\right] - B_{n\gamma}\left[\frac{\alpha(1 - \beta\alpha)m(\ln 10)}{2n}\right] \quad (9)$$

$A_\gamma$ 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[4]), $B_{1\gamma}$ and $B_{n\gamma}$ are Guggenheim ion-interaction parameters for counterion association with monomer $\mathrm{R{-}OCH_2CH_2OSO_3^-}$ and with $n$-mer with partially neutralized charged $(\mathrm{Na^+})_{n\beta}(\mathrm{R{-}OCH_2CH_2OSO_3})_n^{-n(1-\beta)}$, respectively.

The ionic strength, $I$, is determined from eq 10 where $\delta$ is a screening factor introduced to reduce the charge on the aggregate.

$$I = \frac{[2(1 - \alpha) + n\delta^2(1 - \beta)^2\alpha + (1 - \beta)\alpha]m}{2} \quad (10)$$

The function $\sigma(y)$ in eq 9 is defined by eq 11

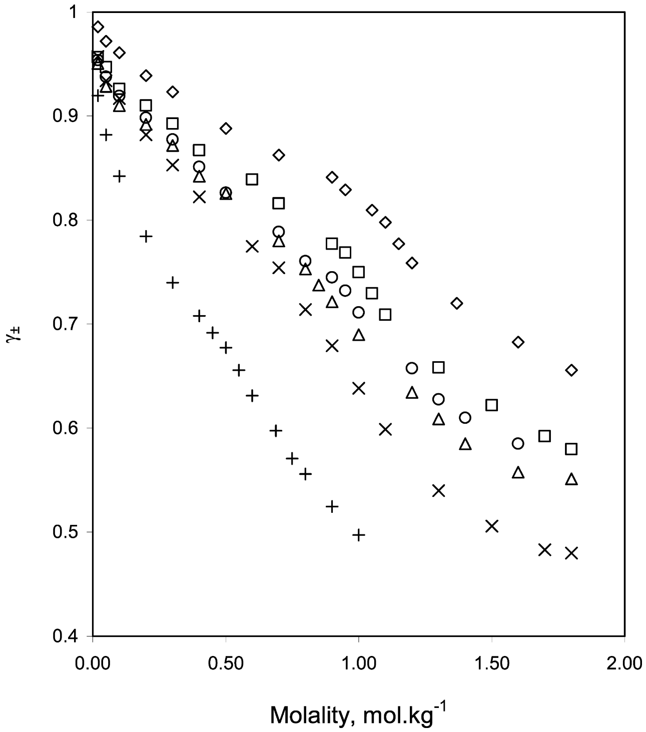

**Figure 4.** $\gamma$ as a function of hydrotrope concentration at 40 °C: ◇, NaMMGS; □, NaEMGS; Δ, NaPMGS; ×, NaBMGS; ○, NaMDGS; +, NaBDGS.

$$\sigma(y) = \frac{3[1 + y - 1/(1 + y) - 2\ln(1 + y)]}{y^3} \quad (11)$$

This model was tested against the experimental data by taking $n = 2$ to $n = 50$ for each hydrotrope. The values of the aggregation number ($n$) obtained from the model for NaMMGS, NaEMGS, NaPMGS, NaBMGS, NaMDGS, and NaBDGS are given in Table 4.

Between $\delta = 0.45$ and $\delta = 0.7$, the value of $\beta$ is not very sensitive to the choice of $\delta$ used to fit the data. Hence, the osmotic coefficient data have been fitted to the Burchfield and Woolley model with $\delta = 0.5$ and $\delta = 1$. An example of such a plot is given for NaBDGS at 40 °C in Figure 6. It is apparent from Figure 6 that using $\delta = 1$ the model slightly overestimates the effective charge on the aggregate. Using $\delta = 0.5$, the data give a better agreement with the experimental osmotic coefficient data. The curves in Figure 5 show the osmotic coefficients predicted from the Burchfield−Woolley model for all the hydrotropes using $\delta = 0.5$. It is apparent from the figure that using $\delta = 0.5$ the model successfully estimates the effective charge on the hydrotrope aggregate.

The values of the model parameters, $B_{1\gamma}$ and $B_{n\gamma}$, are summarized in Table 4. For each hydrotrope, the estimated

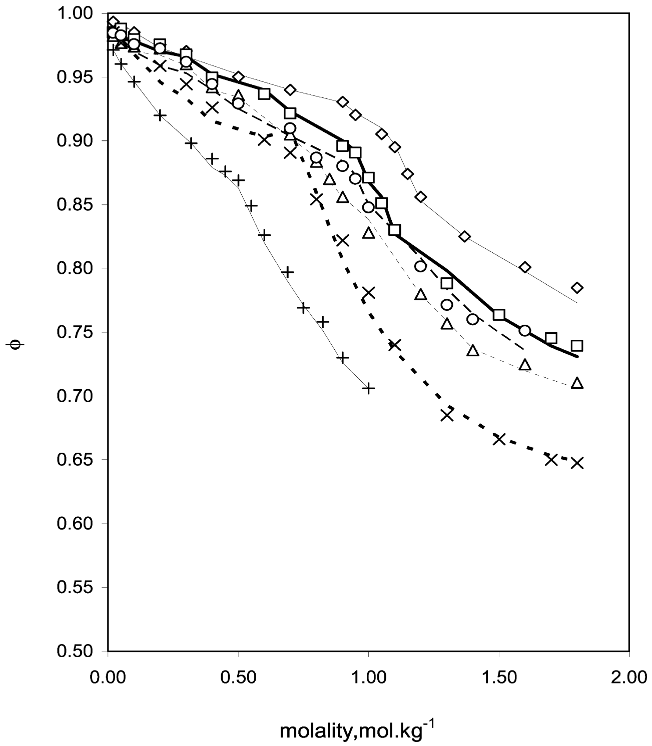

**Figure 5.** $\phi$ as a function of hydrotrope concentration at 40 °C: ◇, NaMMGS; □, NaEMGS; Δ, NaPMGS; ×, NaBMGS; ○, NaMDGS; +, NaBDGS.

**Table 4. MHCs and Burchfield and Woolley Model Parameters, $B_{1\gamma}$/kg·mol$^{-1}$ and $B_{n\gamma}$/kg·mol$^{-1}$, for Hydrotropes at 40 °C, 45 °C, and 50 °C**

| | MHC | | 40 °C | | 45 °C | | 50 °C | |
|---|---|---|---|---|---|---|---|---|
| | mol·kg$^{-1}$ | $n$ | $B_{1\gamma}$ | $B_{n\gamma}$ | $B_{1\gamma}$ | $B_{n\gamma}$ | $B_{1\gamma}$ | $B_{n\gamma}$ |
| NaBMGS | 0.80 | 6 | −0.075 | 3.02 | −0.079 | 3.04 | −0.079 | 3.12 |
| NaPMGS | 0.85 | 9 | −0.061 | 2.74 | −0.065 | 2.76 | −0.069 | 2.77 |
| NaEMGS | 0.95 | 13 | −0.048 | 1.33 | −0.048 | 1.58 | −0.050 | 1.59 |
| NaMMGS | 1.10 | 16 | −0.046 | 0.77 | −0.047 | 0.78 | −0.046 | 0.80 |
| NaBDGS | 0.50 | 17 | −0.076 | 6.68 | −0.084 | 7.25 | −0.099 | 8.01 |
| NaMDGS | 0.95 | 8 | −0.049 | 1.31 | −0.049 | 1.34 | −0.056 | 1.35 |

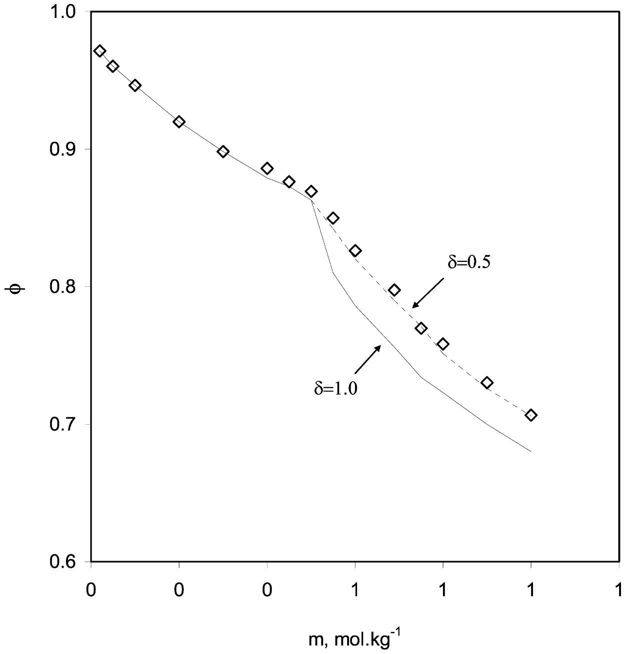

**Figure 6.** $\phi$ as a function of NaBDGS concentration at 40 °C: ◇, Experimental; - - -, $\delta = 0.5$; —, $\delta = 1$.

values for $B_{1\gamma}$ were not very significant. In previous investigations involving sodium alkane 1-sulfonates[22] and alkyl trimethylammonium bromides,[23] only $B_{n\gamma}$ was sufficient to describe the osmotic coefficients using the Burchfield−Woolley model. NaBDGS shows a comparatively greater extent of counterion binding with the aggregate among all glycol/carbitol sulfate hydrotropes and hence increased counterion−aggregate interactions as reflected in the $B_{n\gamma}$ values which decrease in the order of NaBMGS > NaPMGS > NaMDGS > NaEMGS > NaMMGS. These results indicate that interactions between the hydrotrope aggregates and the counterions are more significant when compared with those between the hydrotrope monomer and its counterion.

## Conclusion

Alkyl glycol and alkyl carbitol sulfates, from their conductometry and vapor pressure osmometry measurements, show mild aggregation behavior in water. The local polynomial regression method has been used successfully to determine the MHCs of all six hydrotropes. Osmotic coefficients for aqueous solutions of NaMMGS, NaEMGS, NaPMGS, NaBMGS, NaMDGS, and NaBDGS also show the aggregating tendency of the hydrotropes with increasing number of aggregates with concentration. The well-defined breaks in plots of $\Phi$ vs ($m$) correspond to the respective minimum hydrotrope concentrations of these hydrotropes. The Burchfield and Woolley model for aggregation of surfactants describes the activity and osmotic coefficient data well for all the hydrotropes over a wide range of concentrations to yield the corresponding specific ion-interaction parameters.

## Literature Cited

(1) Sadvilkar, V. G.; Khadilkar, B. M.; Gaikar, V. G. Aqueous Solutions of Hydrotropes as Effective Reaction Media for the Synthesis of 4-Aryl-1,4-dihydropyridines. *J. Chem. Tech. Biotechnol.* **1995**, *63*, 33.

(2) Gaikar, V. G.; Sharma, M. M. Extractive separations with Hydrotropes. *Sol. Extr. Ion Exch.* **1986**, *4*, 839.

(3) 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.

(4) Burchfield, T. E.; Woolley, E. M. Model for Thermodynamics of Ionic Surfactant Solutions. 1. Osmotic and Activity Coefficients. *J. Phys. Chem.* **1984**, *88*, 2149.

(5) Bauduin, P.; Renoncourt, A.; Kopf, A.; Touraud, D.; Kunz, W. Unified concept of solubilization in water by hydrotropes and cosolvents. *Langmuir* **2005**, *21*, 6769–6775.

(6) Gaikar, V. G.; Wagle, V. B. Osmotic and Activity Coefficients of short chain Alkyl Benzene Sulfonates by Vapor Pressure Osmometry. *J. Chem. Eng. Data* **2006**, *51*, 886.

(7) Thomas, W. V. Quantifying measurement uncertainty in analytical chemistry- a simplified approach; NIST: Gaithersburg, MD 20899-8393.

(8) 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.

(9) Lianos, P.; Lang, J. Static and Dynamic Properties of Sodium p-(1-Propynyl) benzene sulfonate micelles. *J. Colloid Interface Sci.* **1983**, *96*, 222.

(10) Mukerjee, P. The nature of association equilibria and hydrophobic bonding in aqueous solutions of associated colloids. *Adv. Colloid Interface Sci.* **1967**, *1*, 241–275.

(11) Chen, L. J.; Lin, S. Y.; Huang, C. C. Effect of hydrophobic chain length of surfactants on enthalpy-entropy compensation of micellization. *J. Phys. Chem. B* **1998**, *102* (22), 4350–4356.

(12) del Castillo, J. L.; Czapkiewicz, J.; Rodriguez, J. R.; Tutaj, B. Micellar properties of alkydimethylammonium bromides in water. *Colloids Poly. Sci.* **1999**, *277* (1999), 422–427.

(13) González-Pérez, A.; Czapkiewicz, J.; Del Castillo, J. L.; Rodríguez, J. R. Micellar properties of long-chain alkyldimethylbenzylammonium chlorides in aqueous solutions. *Colloids Surf., A: Physicochem. Eng. Aspects* **2001**, *193* (1−3), 129–137.

(14) del Castillo, J. L.; Czapkiewicz, J.; Gonzalez Perez, A.; Rodrıguez, J. R. Micellization of decyldimethylbenzylammonium chloride at various temperatures studied by densitometry and conductivity. *Colloids Surf., A: Physicochem. Eng. Aspects* **2000**, *166*, 161–178.

(15) Kochurova, N. N.; Dmitrovskaya, M. V.; Airapetova, E. R.; Korotkikh, O. P.; Abdulin', N. G. Physicochemical properties of low-dimension systems: Micellar solutions of surfactants and surfactant/polymer complexes. *Russ. J. Gen. Chem.* **2007**, *77* (3), 350–353.

(16) Lopez Fontan, J. L.; Costa, J.; Ruso, J. M.; Prieto, G.; Sarmiento, F. A nonparametric approach to calculate critical micelle concentrations: the local polynomial regression method. *Eur. Phys. J. E.* **2004**, *13*, 133.

(17) Phillips, J. N. Energetics of micelle formation. *Trans. Faraday Soc.* **1955**, *51*, 561.

(18) Fan, J.; Gijbels, I.; Hu, T.-C.; Huang, L.-S. A study of variable bandwidth selection for local polynomial regression. *Statistica Sin.* **1996**, *6*, 113.

(19) Silverman, B. W. *Density estimation for statistics and data analysis*; Chapman and Hall: New York, 1986.

(20) 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.

(21) De Lisi, R.; Ostiguy, C.; Perron, G.; Desnoyers, J. E. Complete Thermodynamic Properties of Nonyl and Decyl Trimethyl Ammonium Bromides in Water. *J. Colloid Interface Sci.* **1979**, *71*, 147.

(22) Dearden, L. V.; Woolley, E. M. Osmotic Coefficients and Enthalpies of Dilution of Aqueous Sodium n- Alkane Sulphonates at the Temperatures (298.15, 313.15, 328.15 and 343.15) K. *J. Chem. Thermodyn.* **1996**, *28*, 1283.

(23) Dearden, L. V.; Woolley, E. M. Osmotic Coefficients of tri methyl ammonium bromides in water and in aqueous sodium bromide solutions at 55°C. *J. Phys. Chem.* **1987**, *91*, 2404.

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