

# Phase Behavior and Spectroscopic Properties for Ternary Systems Water + Sodium Chloride + Diethylene Glycol Monobutyl Ether at 303.15 K and Atmospheric Pressure

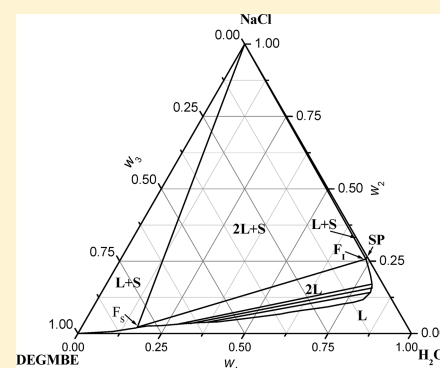
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**S** Supporting Information

**ABSTRACT:** Liquid–liquid–solid equilibria for the ternary system water + sodium chloride + diethylene glycol monobutyl ether have been measured at 303.15 K. The binodal curve and tie lines together with the complete phase diagram have been determined. The fluorescence emission of pyrene in aqueous solution of diethylene glycol monobutyl ether was recorded in a Hitachi F-4500 spectrofluorometer at room temperature with the purpose of investigating the polarity change of solution environment with or without salt. UV–vis spectra for an aqueous solution of diethylene glycol monobutyl ether with different salt concentrations were recorded in a TU1901 UV–vis spectrophotometer. Viscosities were also measured for a 0.08 mass fraction aqueous solution of diethylene glycol monobutyl ether with different concentrations of salt to investigate the salt effect at 303.15 K. The results indicate that molecular interaction between diethylene glycol monobutyl ether and water becomes weaker by the addition of salt.



## INTRODUCTION

Alkoxyethanols are a very interesting class of solvents due to the presence of the ether, alcohol, and hydrocarbon chain in the same molecule.<sup>1</sup> This characteristic leads to self-association behavior of alkoxyethanols in water via the formation of intra- and intermolecular hydrogen bonds. Thus, they are used in various biotechnical and biomedical applications, constituting a simple model of biological systems.<sup>2</sup> They can also be used as a valid model for the research of the hydration of polyether.<sup>3</sup> On the other hand, alkoxyethanols find wide use as important industrial solvents such as scrubbing liquids in the cleaning of exhaust air and gas streams from industrial production plants.

In our previous studies,<sup>4–10</sup> we have measured densities and viscosities for aqueous solutions of several alkoxyethanols at different temperatures with the purpose of obtaining accurate thermophysical property data which is required in process design. These investigations with the help of spectroscopic techniques supply useful information to understand the intermolecular interaction and molecular aggregation that exist in binary liquid mixtures and their sensitivities to composition, temperature, and the molecular structure of the pure components.<sup>11</sup>

Based on this research, we try to investigate the effect of salt on the viscosity of diethylene glycol monobutyl ether (DEGMBE) aqueous solution. Phase separation occurs during the addition of limited amount of NaCl into the aqueous solution with a high mass fraction of DEGMBE. This unexpected phenomenon intrigues us to investigate phase

behavior for the ternary systems water + sodium chloride + DEGMBE.

The salt in mixed solvent plays an important role in scientific research and chemical industry.<sup>12</sup> The addition of a salt to a solvent mixture will modify the interaction among the various solvent and solute molecules which can alter the equilibrium behavior. This phenomenon can be explained by the fact that, by solvating ions, some of water becomes unavailable, and therefore, the solute tendency from aqueous phase to organic phase is favored.<sup>13,14</sup> Liquid–liquid equilibria for a ternary system containing one salt and two solvents are of interest for many unit operations, such as extractive fermentation,<sup>13</sup> extractive crystallization,<sup>15,16</sup> and aqueous two-phase extraction.<sup>17</sup>

As far as we know, there is no report on the phase behavior for the ternary system water + NaCl + DEGMBE. In this work, we measured the liquid–liquid–solid equilibrium data for the ternary system at 303.15 K. The effect of salt on the spectroscopic properties of the studied system was also investigated.

## EXPERIMENTAL SECTION

**Materials.** Diethylene glycol monobutyl ether (DEGMBE, CAS 112-34-5), also called 2-(2-butoxyethoxy) ethanol, was

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purchased from Sinopharm Chemical Reagent Corp. Ltd., and its mass fraction purity was > 99 %. Prior to measurements, it was dried over 0.4 nm molecular sieves and partially degassed under vacuum. Pyrene (CAS 129-00-0) was purchased from Acros with mass fraction purity of 98 %. Pyrene was recrystallized from ethanol before use. Sodium chloride purchased from Sinopharm Chemical Reagent Corp. Ltd. (mass fraction purity > 99.5 %) was dried at 473 K for five hours before use. Doubly distilled water was used.

**Apparatus and Procedure.** The binodal curve was determined by the titration method (cloud point method). A sodium chloride solution of known concentration was titrated with DEGMBE until the clear solution turned turbid. The composition of the mixture can be calculated through weighing the mass of sodium chloride solution and the mass of DEGMBE added by electronic analytical balance (HANGPING FA2104, Shanghai, China) with a precision of  $\pm 0.0001$  g. The temperature was controlled to  $303.15 \pm 0.1$  K in a water bath.

To determine the tie line data, including eutectic points, ternary mixtures of known overall composition lying within the two-phase or three-phase zone were prepared by mass. The mixtures were stirred for 2 h in thermostatic equilibrium and then left to stand and equilibrate for about 24 h. Samples of the conjugate phase were withdrawn, and their compositions were analyzed.

The concentration of salt in both the aqueous phase and the organic phase can be obtained by the evaporation of a known mass of sample. The uncertainty in the measurement was  $\pm 0.8$  %.

The concentrations of DEGMBE and water in the conjugate phase were determined by gas chromatograph. An Agilent 6890N gas chromatograph with a  $2 \text{ m} \times 1/8$  in. Porapak Q packed column and a TCD linked to a HP6890 workstation was used. The carrier gas was hydrogen (flow rate 50 mL/min). The oven temperature was 513.15 K. An injection volume of 1  $\mu\text{L}$  was chosen where the injections were repeated at least three to four times, and the average results were reported. A ball of glass wool was put inside the inlet to prevent the pollution of salt on the GC column. The external standard method was used for the calibration of the gas chromatograph. A series of standards with known compositions were prepared and analyzed, and the mass fraction ratios for DEGMBE/water were regressed to the corresponding peak area ratios. The results indicated that the maximum relative error between the measured and true composition was 0.2 % mass.

The solid phase in equilibrium with the liquids was anhydrous sodium chloride, which can be determined by comparing its thermogravimetric analysis curve with that of pure sodium chloride.

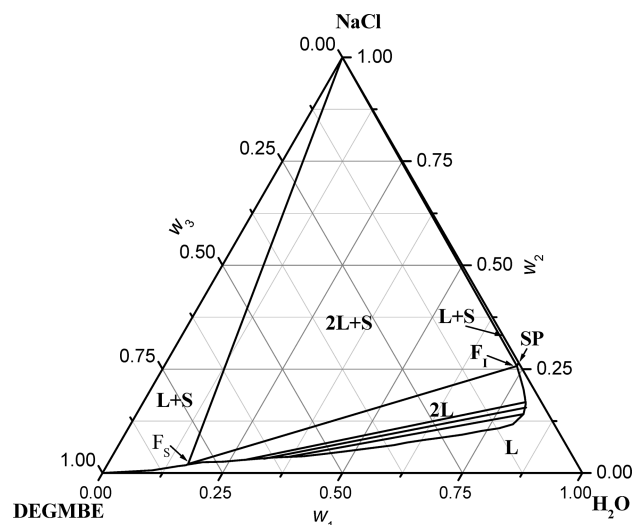
The measurements for investigating the solution polarity by using the pyrene  $I_1/I_3$  ratio method have been described elsewhere.<sup>5,18,19</sup> A predetermined amount of  $5 \cdot 10^{-2} \text{ mol} \cdot \text{cm}^{-3}$  pyrene acetone solution was input into sample bottles, and then acetone was evaporated, followed by the addition aqueous solution of DEGMBE with various concentrations. The salt content added to the sample was fixed at  $0.85 \text{ mol} \cdot \text{kg}^{-1}$ . The concentration of pyrene in each sample solution was maintained to be  $1 \cdot 10^{-3} \text{ mol} \cdot \text{cm}^{-3}$ . The aqueous solutions were stirred overnight for equilibration prior to measurements. Fluorescence emission was recorded in a Hitachi F-4500 spectrofluorometer at room temperature with an excitation wavelength of 335 nm. The slit width was kept at 2.5 nm during measurements.

UV–vis spectra for aqueous solution of DEGMBE with different composition were recorded on a TU-1901 UV–vis spectrophotometer by using 1 cm quartz cuvette covering the region of (190 to 350) nm. A baseline correction was made for the spectra recorded in deionized water.

The methods for density and viscosity measurements had been described previously.<sup>4</sup> Ternary mixtures were prepared by mass, using an electronic analytical balance. The densities of the pure liquids and the mixtures were measured with a 10  $\text{cm}^3$  capillary pycnometer. The viscosities were determined with a capillary viscometer of Ubbelohde type. Degassed pure water was used as calibrating substances. The experimental temperature was controlled to  $\pm 0.01$  K by using a water bath. The uncertainty of the density and viscosity measurements was estimated to be  $\pm 0.1\%$  and  $\pm 0.3$  %, respectively.

## RESULTS AND DISCUSSION

Figure 1 shows the complete phase diagram for the studied ternary systems plotted on triangular coordinates at 303.15 K.



**Figure 1.** Complete phase diagram for water (1) + sodium chloride (2) + DEGMBE (3) at 303.15 K in triangular coordinates. L, liquid phase; 2L, two coexisting liquid phases; 2L + S, two coexisting liquid phases and a solid phase; L + S, a liquid phase and a solid phase; SP, solubility point of NaCl in water; F<sub>1</sub> and F<sub>2</sub>, eutectic points in the bottom and top phases, respectively.

There are five zones in the phase diagram in which the letter L and S denote the liquid and solid phases, respectively.

Region L represents homogeneous unsaturated solution.

The biphasic zone labeled 2L represents two coexisting liquid phases in equilibrium, the top phase rich in DEGMBE and the bottom phase rich in water.

Mixtures represented by points within region 2L + S will separate into two immiscible liquid phases in equilibrium with a solid phase NaCl. In this zone, the composition of each liquid phase remains constant while the relative amount of the solid and two liquids will change depended on the lever rule.

Two L + S regions are observed, where the solid phase of anhydrous NaCl is in equilibrium with the saturated solution. The right region is very narrow. The saturation curve of right region is from point SP, the solubility point of NaCl in water, to point F<sub>1</sub>, the eutectic point of the bottom phase. While the saturation curve of left region is from point F<sub>2</sub>, the eutectic

point of the top phase, to the vertex point of pure DEGMBE. Salt has negligible solubility in pure DEGMBE.

The binodal curve data for ternary system water + sodium chloride + DEGMBE at 303.15 K are listed in Table 1. The

**Table 1. Binodal Data as Mass Fraction for Water (1) + Sodium Chloride (2) + DEGMBE (3) at 303.15 K**

100 $w_1$	100 $w_2$	100 $w_3$	100 $w_1$	100 $w_2$	100 $w_3$
10.02	0.68	89.30	59.74	7.36	32.9
14.99	1.65	83.36	63.26	8.01	28.73
16.41	1.91	81.68	66.12	8.46	25.42
16.57	2.03	81.39	70.40	9.24	20.36
19.54	2.58	77.88	73.92	10.14	15.94
23.77	2.75	73.48	77.25	10.75	12.00
28.16	3.19	68.65	79.65	11.75	8.60
33.78	3.74	62.48	80.29	13.21	6.50
39.86	4.01	56.13	80.61	14.24	5.15
43.55	4.55	51.90	79.92	16.59	3.49
47.51	5.15	47.34	79.02	18.08	2.90
52.78	6.01	41.21	77.65	20.15	2.20
57.33	6.72	35.95	75.59	22.99	1.42

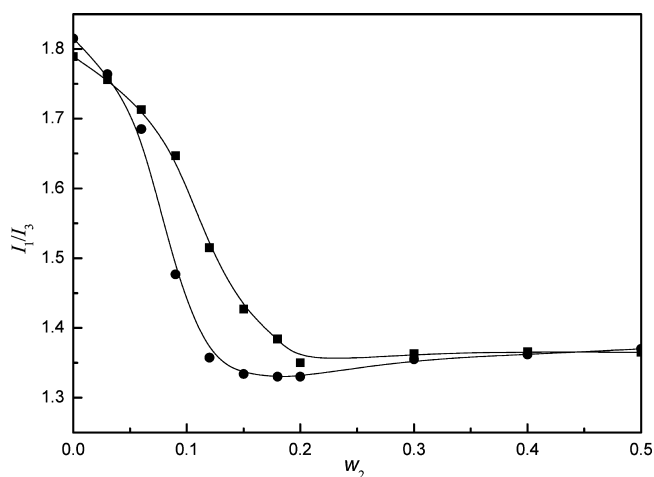
compositions of tie lines together with the eutectic points of the top and bottom phases at 303.15 K are given in Table 2.

**Table 2. Tie Line Data as Mass Fraction for Water (1) + Sodium Chloride (2) + DEGMBE (3) at 303.15 K**

top phase			bottom phase		
100 $w_1$	100 $w_2$	100 $w_3$	100 $w_1$	100 $w_2$	100 $w_3$
36.68	3.87	59.45	80.52	14.14	5.34
31.92	3.44	64.64	80.38	15.76	3.86
28.05	3.11	68.84	79.67	17.05	3.28
16.76 <sup>a</sup>	2.22 <sup>a</sup>	81.02 <sup>a</sup>	73.47 <sup>b</sup>	25.76 <sup>b</sup>	0.77 <sup>b</sup>

<sup>a</sup>The eutectic point of the top phase. <sup>b</sup>The eutectic point of the bottom phase.

As shown in Figure 2, the  $I_1/I_3$  ratio decreases sharply as the mass fraction  $w_2$  of DEGMBE increases in the water-rich region with or without salt. The value of  $I_1/I_3$  ratio reaches a minimum

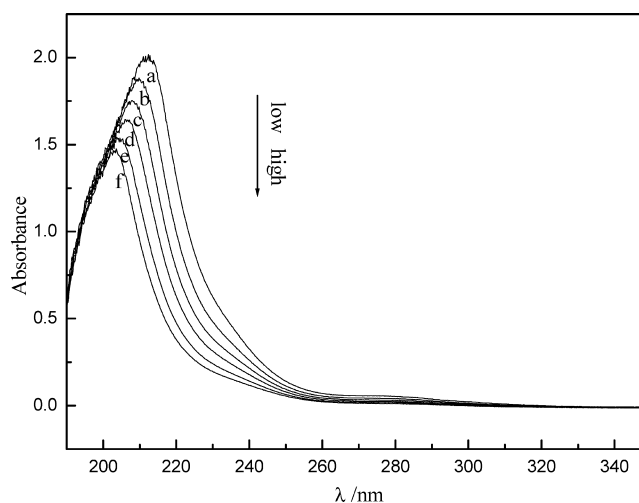


**Figure 2.** Fluorescence emission intensity ratio  $I_1/I_3$  vs mass fraction  $w_2$  of DEGMBE for water (1) + DEGMBE (2) at room temperature: ■, 0 mol·kg<sup>-1</sup> NaCl; ●, 0.85 mol·kg<sup>-1</sup> NaCl.

around  $w_2 = 0.2$ , then increases slowly. It can also be observed that the  $I_1/I_3$  ratio for DEGMBE solution with 0.85 mol·kg<sup>-1</sup> NaCl is smaller than that without salt before  $w_2 < 0.3$ , while there is no significant difference for  $I_1/I_3$  ratio when  $w_2 > 0.3$ . It indicates that the polarity of environment where pyrene is located decreases sharply in water-rich region. Therefore we can suppose that the aggregation of DEGMBE occurs, which leads to a lower polarity environment preferred by pyrene.

Durov et al.<sup>20</sup> had proposed the model of aggregation including chain-like aggregates and cyclic tetramers of ethanol in dioxane–ethanol mixtures. The existence of salt can enhance the aggregation behavior of DEGMBE in the water-rich region.

UV–vis spectroscopy gives information about various electronic transitions. Figure 3 shows that blue shift phenomena happened with increasing water content for an

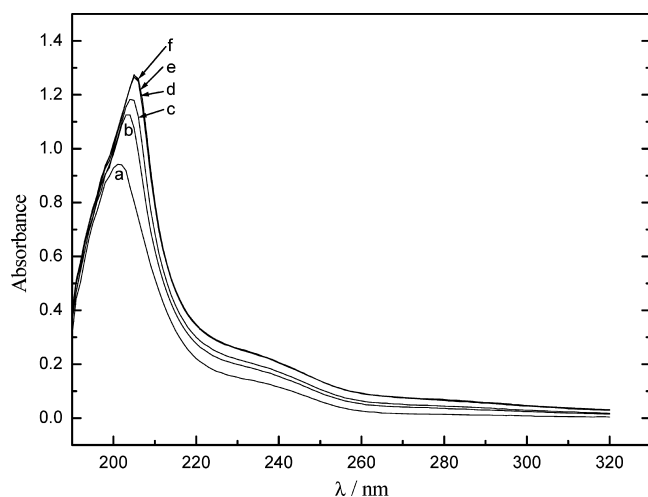


**Figure 3.** UV–vis absorption spectra of binary system water + DEGMBE with a varied mass fraction of water at room temperature: a, 0.799; b, 0.819; c, 0.838; d, 0.853; e, 0.868; f, 0.881.

aqueous solution of DEGMBE without salt. It may be attributed to the electronic transitions of the lone pairs of ether oxygen and hydroxyl oxygen atom,  $n \rightarrow \sigma^*$  electronic transitions. With increasing water content, hydrogen bond interaction between DEGMBE and water happens easily. The interaction makes the electronic transition of the lone pairs difficult.

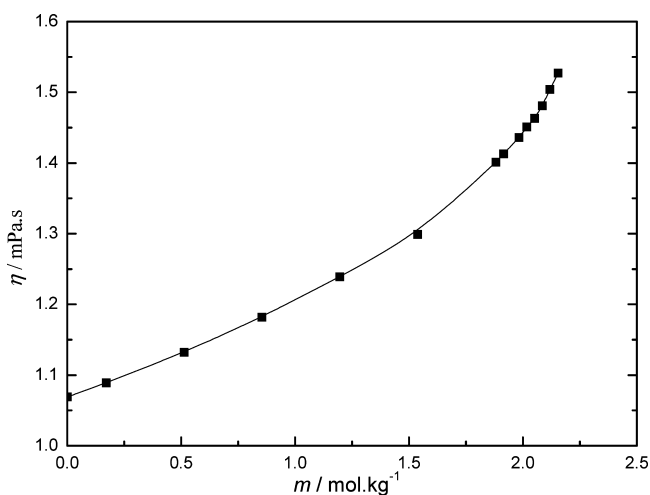
Figure 4 shows that red shift phenomena occurred and the peak value also increased for aqueous solution of DEGMBE with its mass fraction fixed at 0.04 by increasing the salt content, (0, 0.34, 0.68, 1.03, 1.37, and 1.71) mol·kg<sup>-1</sup>. It can be observed that the further addition of salt has almost no effect when the concentration of salt reaches near 1.03 mol·kg<sup>-1</sup>. Thus we can suggest that the bonding ability of salt ion with water is stronger than the bonding ability of DEGMBE with water. The addition of salt which destructs part of the hydrogen bonds between water and DEGMBE makes it easy for the electronic transitions of the lone pairs of ether oxygen and hydroxyl oxygen atom,  $n \rightarrow \sigma^*$  electronic transitions. Thus the peak value increases with increasing salt content accompanied by a red shift.

To investigate the effect of salt on the viscosity for aqueous solution of DEGMBE, the mass fraction of DEGMBE was fixed at 0.08 which permits adequate solubility of NaCl. Experimental results of density and viscosity are provided in



**Figure 4.** UV-vis absorption spectra of DEGMBE aqueous solution with the mass fraction of DEGMBE  $w_2 = 0.04$  at room temperature: a, 0 mol·kg<sup>-1</sup> NaCl; b, 0.34 mol·kg<sup>-1</sup> NaCl; c, 0.68 mol·kg<sup>-1</sup> NaCl; d, 1.03 mol·kg<sup>-1</sup> NaCl; e, 1.37 mol·kg<sup>-1</sup> NaCl; f, 1.71 mol·kg<sup>-1</sup> NaCl.

the Supporting Information. Figure 5 is the plot of viscosity for aqueous solution of DEGMBE against the concentration of



**Figure 5.** Viscosity vs NaCl concentration  $m$  for water (1) + DEGMBE (2) with the mass fraction of DEGMBE  $w_2 = 0.08$  at 303.15 K.

NaCl. It can be observed that the viscosity increases with increasing the concentration of NaCl. On the basis of the fact that the viscosity of aqueous solution of NaCl increases linearly as the concentration of NaCl increases, it may suggest that the salting-out effect promotes the aggregation of DEGMBE which results in the increase of viscosity.

As a summary of this paper, there exist hydrogen bonds between water and DEGMBE molecules. By solvating salt, each ion binds a constant number of water molecules which become unavailable for DEGMBE, and phase separation will occur as the amount of salt increases. It is obvious that the interaction between salt ions and water is stronger than that between DEGMBE and water. Spectroscopic properties as well as viscosity studies supply further information to insight in the interaction among water, DEGMBE, and salt.

## ■ ASSOCIATED CONTENT

### 📄 Supporting Information

Experimental results of density and viscosity for the mixture of water + DEGMBE with the fixed mass fraction of DEGMBE 0.08 while increasing the NaCl content at 303.15 K. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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