bonding, whereas the negative values of $\delta(\Delta k_s)/\delta T$ for the system CH_2ClCH_2Cl–benzene can be visualized to be due to the predominance of the contributions to Δk_s from nonspecific interactions over those from specific interactions.

Acknowledgment

We are extremely grateful to Professor S. C. Tripathi, Head of the Chemistry Department, Gorakhpur University, Gorakhpur, for encouragement during the course of this investigation.

Registry No. CH_2ClCH_2Cl, 107-06-2; benzene, 71-43-2; toluene, 108-88-3; *p*-xylene, 106-42-3; quinoline, 91-22-5; cyclohexane, 110-82-7.

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Solubility and Metastable Zone Width of Sodium Chloride in Water–Diethylene Glycol Mixtures

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The solubility of sodium chloride in aqueous diethylene glycol (DEG) was determined in the range of 0–100% DEG concentration and 10–90 °C. The temperature–solubility relationships can be expressed by straight lines, whose parameters are functions of the solvent composition and can be predicted by second-order expressions. The temperature coefficient of the solubility varies progressively, being negative for solutions 100–74 wt % of DEG, and positive for solutions 74–0 wt % of DEG. The metastability range in 0–100% aqueous DEG was also determined: it becomes wider on increasing the DEG content in the solvent.

Introduction

During the dehydration of crude natural gas, usually performed with concentrated solutions of ethylene glycols, significant amounts of salts may accumulate in the liquid phase. In order to prevent excessive scaling over the heat-transfer surfaces of the dehydration loop, it is very important to know the solubility characteristics of these salts in the particular solvent. The predominant salt is sodium chloride: its solubilities in mixtures of water–diethylene glycol (DEG) are reported in some published papers (*1–6*). However, the data are not complete, being limited either to a partial range of solvent compositions (mixtures rich of DEG) (*1–4*), or to room temperature alone (*5*, *6*). Moreover, while the dependence of the temperature–solubility coefficient on the solvent composition is qualitatively confirmed, from the quantitative point of view significant discrepancies appear; in fact for 80 wt % of DEG both negative (*1–3*) and positive (*4*) values are reported. Finally, no data seem to be available about the metastability range. In this work the solubility of sodium chloride in aqueous solutions of DEG has been investigated for water/DEG ratios 0–100% and in a wide interval of temperatures (10–90 °C); in addition the metastability range width has been determined.

Experimental Method

All the chemicals were Farmitalia Carlo Erba with the following purities: sodium chloride >99.5%, diethylene glycol >99.5%, and water bidistilled grade.

The experimental apparatus was a 250-mL cylindrical jacketed glass cell, connected to a thermostatic bath and magnetically stirred. Temperature was maintained and read with a precision of ±0.1 °C.

(*I*) ***Solubility***. The two methods commonly adopted (*7*) to determine solubility data have been used. The first, which consists of increasing and decreasing the temperature of a solution prepared from weighed amounts of salt and solvent till nucleation or dissolution take place, has been found unsuitable, especially for solvent compositions in the range 80–50 wt % of DEG where the temperature exhibits little or no influence over sodium chloride solubility: measurements were carried out according to this first method only for 100% DEG solvent.

The second method consists of maintaining at a fixed temperature a stirred solution containing some excess of salt till equilibrium conditions are reached, and afterwards measuring the concentration of the saturated solution. In the present case the salt content was determined by applying the gravimetric method to samples (about 10 mL each) withdrawn from the solution. The precision of the gravimetric method was tested by determining the solids recovery with water–DEG solutions containing weighed amounts of sodium chloride: the standard deviation obtained was <0.04 g of NaCl/100 g of solvent.

Liquid and solid phases were assumed to be in equilibrium when the differences between the salt content of the liquid determined in three consecutive samples withdrawn at about 6-h intervals was within 0.08 g of NaCl/100 g solvent. The sampling procedure was as follows. Stirring was stopped and the crystals were allowed to settle for 15–30 min, depending on the viscosity of the solution, which is principally affected by the DEG concentration; three samples were withdrawn by

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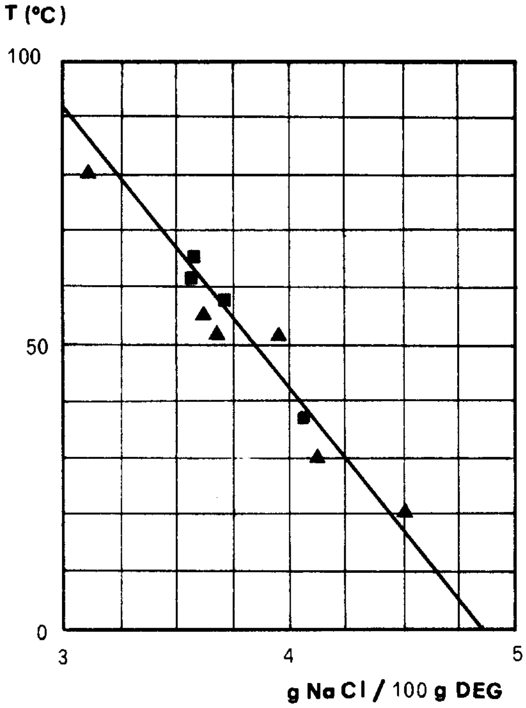

Figure 1. Solubility of NaCl in DEG: ■, first method; ▲, second method.

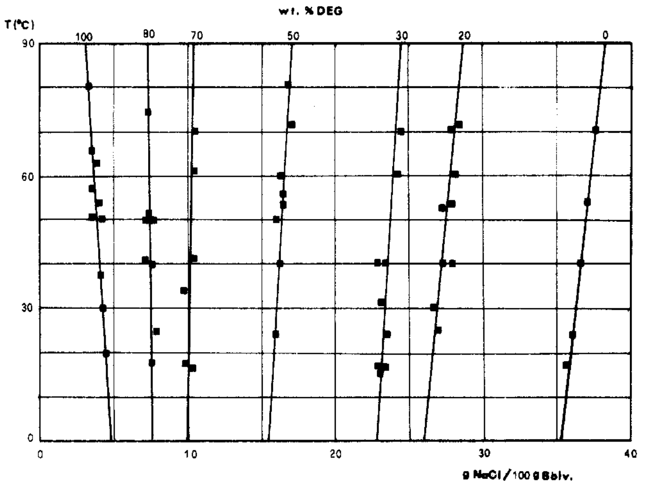

Figure 2. Solubility of NaCl in water-DEG mixtures.

Table I. Solubility of Sodium Chloride in Water-DEG Mixtures

wt % DEG	temp, °C	solubility[a]	wt % DEG	temp, °C	solubility[a]
100	20.0	4.49	50	54.4	16.65
100	30.0	4.11	50	56.2	16.60
100	37.5	4.05	50	59.6	16.21
100	50.5	3.93	50	72.0	17.04
100	50.8	3.69	50	81.0	16.87
100	55.0	3.68	30	17.0	23.23
100	58.0	3.70	30	18.0	23.13
100	62.3	3.60	30	18.0	23.22
100	64.5	3.59	30	25.0	23.52
100	80.0	3.11	30	31.5	23.39
80	18.0	7.74	30	40.0	22.97
80	25.0	7.92	30	40.0	23.50
80	40.0	7.42	30	60.0	24.31
80	41.0	7.20	30	70.0	24.20
80	50.3	7.68	20	27.0	26.76
80	50.5	7.54	20	30.0	26.79
80	50.5	7.63	20	40.0	27.28
80	75.0	7.31	20	40.0	27.86
70	18.0	10.16	20	50.0	26.89
70	18.5	9.99	20	50.5	27.78
70	35.0	9.76	20	59.6	28.11
70	41.0	10.20	20	70.0	28.08
70	52.0	10.35	20	72.0	28.17
70	70.1	10.25	0	18.0	35.82
50	25.0	16.17	0	25.0	35.94
50	40.0	16.27	0	40.0	36.65
50	50.5	16.20	0	55.0	37.02

[a] Grams of NaCl per 100 g of solvent.

Table II. Parameters of the Solubility Lines

wt % DEG	a	10^3b	sd[a]
100	4.841	−20.57	0.085
80	7.893	−7.71	0.195
70	9.916	5.18	0.184
50	15.673	15.10	0.211
30	22.787	19.99	0.266
20	26.069	29.84	0.348
0	35.168	34.47	0.083

[a] Grams of NaCl per 100 g of solvent.

Table III. Metastability Range

wt % DEG	metastable zone width, °C	wt % DEG	metastable zone width, °C
100	20.0	50	8.9
100	18.5	50	7.4
90	16.1	40	7.2
90	15.1	20	6.0
80	10.1	0	3.5
80	11.5		

means of special double-walled pipets, maintained, up to use, at the same temperature of the solution, in order to avoid any precipitation of solubilization. The samples were immediately weighed; their temperature was then increased up to 300 °C in a very gradual manner, in order to avoid sprinkling during the solvent evaporation.

(II) Metastable Zone Width. The metastable zone is the region between the solubility and the supersolubility curves; in the present work its width was measured by varying the temperature of a clear saturated stirred solution till nucleation takes place (*7*). The stirring rate adopted was 300 rpm, the cooling/heating rate 0.5 °C/min, and the initial temperature 60 °C.

The clear saturated solution used for the metastability range measurements was carefully transferred from a first cell, where it was in equilibrium with the solid salt to a second one, where nucleation takes place. In order to avoid the birth of some nuclei in the transfer of liquor the two cells and the copper connection were maintained at the same temperature; in addition the first cell was provided with a porous filtering glass (diameter of the pore <16 μm) at the exit end in order to block the entrained crystals. The transfer from one cell to the other was realized by slightly pressurizing the first one with dry compressed air.

Results

First of all a good agreement between the solubility data obtained by means of the two methods previously reported is shown for 100% DEG solutions in Figure 1.

The complete sets of solubility determinations carried out in this work are shown in Table I and their respective temperature-solubility curves in Figure 2. The solubility data reported are the mean values of three samples (sd < 0.04). From Figure 2 it can be observed that the solubility data can be fitted by straight lines of the form

$$c = a + bT \qquad (1)$$

where c is the solubility (g of NaCl/100 g of solvent) and T is the temperature (°C). The values of a and b for each solubility line are reported in Table II together with the standard devia-

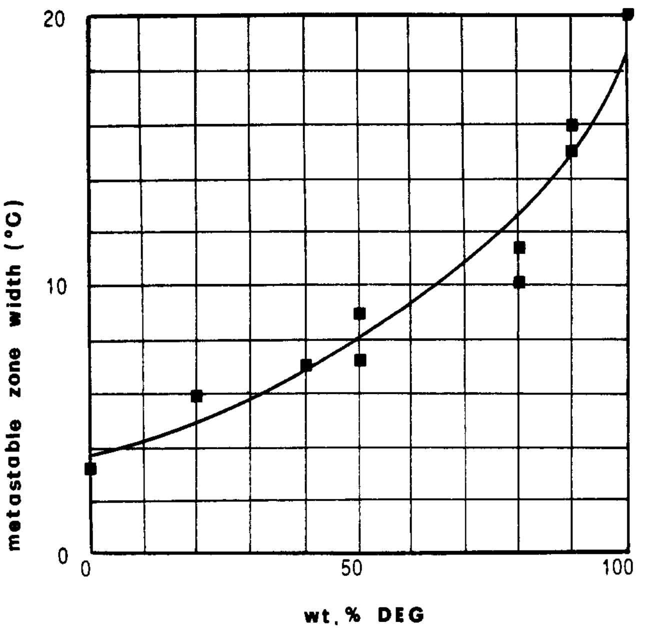

Figure 3. Metastable zone width of NaCl in water-DEG mixtures.

tions between experimental and calculated data. The temperature-solubility coefficient is negative for solvent compositions 100-80 wt % of DEG, and positive for 70-0 wt % of DEG.

The metastable zone width data are reported in Table III; they correspond to a supercooling where the solubility increases with the temperature and to an undercooling in the opposite case. Figure 3 shows the curve of maximum allowed supercooling vs. DEG wt % in the solvent: the reproducibility of the measurements was found as ±0.75 °C. Even though the experimental data are in this case slightly more dispersed than those concerning the solubility, it appears clear that the width of the metastable zone becomes smaller on decreasing the DEG concentration in the solvent. A suitable fitting of these data was obtained by means of an exponential curve.

Discussion

The values of the parameters *a* and *b* of the solubility lines were also correlated to the weight concentration of DEG in the solvent by applying the least-squares method to polynomial expressions: negligible improvements of the correlation index occurred by adopting an order greater than two. The following second-order expressions are therefore proposed

$$a = 35.22 - 0.4806W + 0.001740W^2, \quad \text{g NaCl/100 g solv} \qquad (2)$$

$$10^3 b = 34.42 - 0.2880W - 0.002345W^2, \quad \text{g NaCl/°C 100 g solv} \qquad (3)$$

where *W* is the wt % of DEG in the solvent.

Equations 1-3 allow the prediction of the solubility of sodium chloride for any temperature in the considered range and for any concentration of DEG in the solvent: the standard deviation between the experimental data and those calculated by eq 1-3 is 0.280 g of NaCl/100 g of solvent.

The comparison between the solubility data reported here and those in the literature shows a good agreement with the data of most of the authors (*1-3*, *5*, *6*). The influence of the temperature on the solubility has been confirmed over the whole range of compositions; a single paper (*4*), in fact, reports a positive temperature solubility coefficient for solutions containing 80 wt % of DEG, contrasting with the results of this work and of all the other studies (*1-3*). Solubility-temperature relationships, obtained for solutions 100-70 wt % of DEG (*1*), 100-50 wt % of DEG (*2*), and 100-60 wt % of DEG (*3*) (except for 60 wt % of DEG in ref *3*), are expressed by straight lines as in the present work. The DEG content corresponding to a temperature-solubility coefficient equal to zero is localized at about 70 wt % (*1*, *2*), and 77 wt % (*3*), very close to the value predicted in this work by eq 3 which is 74 wt %. Equations 1-3 obtained here referring to temperatures ranging from 10 to 90 °C give also a good fitting of the measurements carried out by other authors (*1-3*, *5*, *6*): the standard deviation between the calculated and reported data is in the range 0.35-0.1 g of NaCl/100 g of solvent. There are also similar deviations between experimental data presented by different authors. Moreover, referring to the solubility of sodium chloride in water in the examined range of temperatures, eq 1-3, with $W = 0$, offer a reliable prediction: the standard deviation between the calculated data and those reported by the literature (*7-12*) is less than 0.20 g of NaCl/100 g of solvent. Very scarce indications are available about the metastability range width: a maximum supercooling of 1 °C is reported (*8*) for sodium chloride in water adopting a very slow cooling rate (1 °C/h) under "moderate" agitation and in presence of seed crystals. Other data available for aqueous solutions of sodium chloride (*13*) are in the range 1-5 °C for cooling rates ranging from 0.1 to 0.4 °C/min and in presence of seeds too; no information is given by the authors about the stirring rate. In this work a value of 3.5 °C was obtained by adopting a cooling rate of 0.5 °C/min and without adding seeds.

The increase of the metastability range with the increasing of the DEG concentration in the solvent, shown in Figure 3, is associated with the corresponding decrease of the sodium chloride solubility. The dependence of the maximum allowable supersaturation on the solute concentration has been pointed out by Nyvlt (*14*) referring to many inorganic salts in aqueous solutions: as the solute concentration decreases, the aggregation of the particles to give stable clusters becomes more difficult, and, therefore, the metastable zone becomes wider.

The curve shown in Figure 3 has been obtained by fitting the experimental data applying the least-squares method to polynomial and exponential expressions: the following exponential curve gave the best interpolation

$$\Delta T_{\max} = \exp(1.33629 + 0.015135W) \qquad (4)$$

where $\Delta T_{\max}$ is the metastable zone width. The standard deviation between the calculated and experimental data is 1.46 °C.

Conclusions

Sodium chloride in water-DEG mixtures presents solubility-temperature coefficients passing from negative to positive values as the DEG content in the solvent decreases. Two second-order expressions have been proposed which allow a reliable prediction of the solubility at any solvent composition at any temperature between 10 and 90 °C. The metastability range decreases with the increase of the solubility in agreement with other observations reported in the literature (*14*).

Registry No. NaCl, 7647-14-5; DEG, 111-46-6.

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Effect of Additive Gases on the Liquid–Liquid–Vapor Immiscibility of the Carbon Dioxide + *n*-Nonadecane Mixture

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Liquid–liquid–vapor phase equilibria behavior is studied for the ternary mixtures CO_2 + nitrogen + *n*-nonadecane and CO_2 + propane + *n*-nonadecane in an effort to determine the effect of additive gases on the liquid–liquid–vapor behavior seen in the binary mixture CO_2 + *n*-nonadecane. In pressure–temperature space, the ternary three-phase region develops to the low-temperature side of the binary liquid–liquid–vapor locus when nitrogen is added, whereas the addition of propane to the binary mixture results in the three-phase region developing to the high-temperature side of the binary locus. Properties reported are pressure, temperature, and compositions and molar volumes for all three fluid phases in the three-phase regions, in addition to location and characterization of the boundaries of the regions.

Introduction

The authors have undertaken an extensive study of the multiphase equilibria behavior of CO_2 + hydrocarbon mixtures. In an earlier study, the liquid–liquid–vapor (LLV) phase equilibria behavior of the binary mixture CO_2 + *n*-nonadecane was reported (*1*). In this paper, we report how this binary LLV behavior is altered by the addition of a third component, either propane or nitrogen. *n*-Nonadecane exhibits LLV immiscibility with CO_2 over a range of 12.6 K up to 32.3 °C.

There is both economic and scientific interest in how impurities, or "additive gases", affect the phase equilibria of CO_2 + crude oil systems. The ternary system of CO_2 + nitrogen + *n*-nonadecane has relevance to the problem of using nitrogen as an additive gas in a CO_2 flood in an effort to reduce the cost of the pressurizing gas. Also, during a flood the CO_2-rich gas phase in a reservoir can become enriched with light hydrocarbons such as propane after multiple contacting of the live oil. The presence of propane can expand existing three-phase behavior in pressure–temperature space or even induce it at temperatures where it would not have existed if the pressurizing gas were pure CO_2. The phase equilibria data are also useful in assessing, as well as contributing to, the flexibility of an equation of state with respect to the composition of the pressurizing gas, as might be appropriate to a reservoir simulation.

Previous work on liquefied natural gas systems (*2*) has led to an understanding of the manner in which a third component extends the three-phase region from the LLV locus of an originally immisicible binary pair. In pressure–temperature space, the three-phase region will develop to the low-temperature side of the binary locus if the third component is too molecularly dissimilar to be LLV immiscible with either one of the first two components. The ternary system of methane + *n*-hexane + *n*-octane behaves in this manner (*3*) where methane + *n*-hexane is the LLV immiscible binary mixture. This will be the case for the ternary system CO_2 + nitrogen + *n*-nonadecane.

Propane is miscible with both CO_2 and *n*-nonadecane and therefore the three-phase region will extend to the high-temperature side of the binary LLV locus. The system of methane + *n*-hexane + CO_2 is similar in nature (*3*).

Some three-phase composition data for the system of CO_2 + propane + *n*-hexadecane have been reported earlier by Meldrum and Nielsen (*4*), and recently interpreted by Orr and Jensen (*5*). Pressure–composition data are reported at 60 and 70 °F. However, no previous CO_2 + nitrogen + hydrocarbon three-phase studies exist, to the knowledge of the authors.

Experimental Apparatus and Procedures

A description of the experimental apparatus is given in an earlier paper (*6*). Some modifications were necessary to allow the study of ternary systems. These are described in ref *7*. The procedures for performing LLV studies are presented in the same reference. We briefly summarize those procedures; the apparatus employs a stoichiometric approach wherein a known amount of *n*-nonadecane is added to a visual (glass) equilibrium cell. (The volume of these cells is typically 7–8 mL.) Measured amounts of gas are added to the cell from high-pressure bombs. By careful mass balances, the composition and molar volume of the three phases can be determined from conjugate measurements at a given temperature and pressure.

Conjugate measurements involve three experimental runs in which one measurement has a large amount of L_1 relative to the L_2 and V phases. The second measurement has a large amount of L_2 relative to L_1 and V, and the third measurement has a large amount of V relative to L_1 and L_2. The analysis requires that both temperature and pressure be set, which for a ternary three-phase system defines an invariant point. Experimentally, this required the study of isotherms within the three-phase region. Data are taken at various pressures along the isotherm and then plotted. Smoothing these data makes it possible to select specific pressures at that temperature for analysis. The amount of *n*-nonadecane present in the vapor phase was found to be negligible. In subsequent calculations it was assumed that the vapor contained no hydrocarbon. The boundaries of the LLV regions were determined by straightforward visual observation.

Temperature is measured with a Pt-resistance thermometer to an estimated accuracy of ±0.02 K while pressure is mea-

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