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Solubilities of Sodium Chloride in Organic and Aqueous−Organic Solvent Mixtures

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The solubility of sodium chloride in the binary organic or aqueous−organic solvent mixtures methanol + cyclohexane, water + cyclohexanol, and water + benzyl alcohol as well as in the ternary mixtures water + (ethanol or benzyl alcohol) + cyclohexanol at 298.15 K and ambient pressure has been determined using a gravimetric method. The reliability of the measuring principle has been tested by comparing the solubilities of sodium chloride in methanol, ethanol, and (methanol + cyclohexane) to literature values. The data for the system methanol + cyclohexane + sodium chloride, which were measured over the whole concentration range of the solvent mixture, have been fit to a concentration-dependent expression.

Introduction

The solubility of electrolytes such as sodium chloride must be known for designing separation equipment needed for many technical applications, e.g., for desalination processes or in food processing. Furthermore, the knowledge of the solubility limit of inorganic or organic salts is essential for a safe operation of different processing units such as distillation columns, absorption units, or extraction plants. Against this background, the correlation and prediction of thermodynamic and thermophysical properties, e.g., the prediction of phase equilibria, is of great technical interest. Experimental solubility data are thus also necessary as a basis for predicting solubilities of salts in different solvent systems.

Very often, the solution systems of interest consist of inorganic salts dissolved in aqueous or organic solvents or solvent mixtures. While solubility data for water or for a pure organic substance as a solvent are easily available in the literature for a large amount of salts (e.g., Linke, 1958, 1965; Schäfer and Lax, 1962; Stephen and Stephen, 1964; Janz and Tomkins, 1973), data for aqueous−organic or for organic multicomponent solvent mixtures are at present very scarce, obsolete, or not available at all.

To satisfy this need for experimental data, the present publication reports on gravimetric solubility measurements for sodium chloride in some organic and aqueous−organic solvent mixtures over the whole solvent concentration range at 298.15 K and ambient pressure.

Experimental Section

The following solvent/solute systems have been examined in this work:

methanol + cyclohexane + NaCl
water + cyclohexanol + NaCl
water + benzyl alcohol + NaCl
water + ethanol + cyclohexanol + NaCl
water + benzyl alcohol + cyclohexanol + NaCl

Materials. Sodium chloride was supplied by Fluka (puriss. p.a., purity ≥99.5%). Prior to the measurements, the salt was dried under vacuum for at least 24 h at 240 °C. Water was distilled and filtered four times (conductivity $\leq 1\,\mu$S cm^{-1}). The organic solvents (see Table 1) were used without further purification. They were dried with molecular sieves of 3 Å pore diameter supplied by Fluka (Dehydrat Fluka with indicator), which had been activated under vacuum at 240 °C for at least 6 h. The remaining water content of the solvents as given in Table 1 was determined by coulometric titration using a Karl Fischer coulometer (Mettler Toledo, Giessen, Germany; KF Coulometer DL36). Directly before the measurements, all liquids were degassed by ultrasonic treatment and under vacuum.

Table 1. Organic Solvents

solvent	supplier, purity	water content/ ppm
methanol	Roth, Roti Solv. HPLC (≥99.9%)	<80
ethanol	Roth, Rotipuran (≥99.8%)	<20
cyclohexane	Fluka, for residue analysis (≥99.8%)	<5
cyclohexanol	Fluka, puriss. (≥99.0%)	<25
benzyl alcohol	Fluka, puriss. p.a. (≥99.0%)	<20

Experimental Procedure. A gravimetric procedure was used to determine the solubility data presented here. Solid−liquid equilibrium was attained by placing special glass cylinders containing the prepared solution into a shaking bath. The glass cylinders (inner diameter, 35 mm) have a glass sinter plate (Robu Glasfilter-Geräte GmbH, Hattert, Germany; pore diameter, 10−16 μm) directly at the bottom. They are closed by gastight lids screwed onto both ends of the cylinder. The use of glass tubes of different length (70−200 mm) permits the adjustment of the solution volume to the dissolving capacity of the different solvents.

Prior to the measurements, the glass cylinders were dried at 240 °C, until no further mass loss was detected. The predried solvent mixture was prepared by mass on a Sartorius (Göttingen, Germany) LP1200S balance (accuracy, ±1 mg; precision, ±2 mg). For the concentration $\tilde{w}_{1,123}$ of a ternary solvent mixture given as mass percentage of component 1 in relation to the salt-*free* solvent mixture of components 1, 2, and 3, the error due to weighing inaccuracies only can thus be determined to ±0.06 mg/g according to the Gaussian law of error propagation (with $\sigma_{m_{\mathrm{LM}}} = \sqrt{3}\sigma_{m_i} = 5.2$ mg and an exemplary mass of $m_i = 20$ g for each of the three solvent components). Owing to experimental uncertainties such as solvent evaporation during sample handling, the overall accuracy of the concentration of the binary or ternary solvent mixture can thus be given as $\sigma_{\tilde{w}_{1,123}} = 0.2$ mg/g.

The desired amount of salt to achieve a saturated solution was weighed into the cylinder (between 3 and 12 g, depending on the dissolving capacity of the solvent) using a Sartorius (Göttingen, Germany) MC210P balance (accuracy, ±10 μg; precision, ±20 μg). The predried solvent mixture was added, and the cylinder was closed immediately with the gastight lid to minimize losses due to evaporation.

To facilitate the dissolution process, the glass tubes were placed into an ultrasonic bath before being transferred to a thermostated shaking water bath (GFL, Burgwedel, Germany; GFL1086) running at 150 min^{-1}. The bath temperature was maintained constant to ±0.1 K. A shaking time of 48 h had been determined to be sufficient for establishing the solute/solvent equilibrium. To separate the saturated solution from the remaining solute after equilibration, the cylinders were evacuated immediately after being taken out of the shaking water bath using a water-jet vacuum pump attached to the bottom of the glass cylinder. In this way, solubility changes due to a change in temperature were minimized. The undissolved salt remaining on the glass sinter plate was dried at 240 °C. The mass of the dissolved salt, m_s, and thus the concentration w_{sat} of the saturated solution (as mass percentage of salt in the saturated solution) were determined by differential weighing (Sartorius MC210P balance, $\sigma_{m_s} = \sqrt{2}\cdot 30$ μg) with an overall accuracy of $\sigma_{w_{sat}} = 0.5$ mg/g. This value takes into account the accuracy of the solubility as calculated according to the Gaussian law of error propagation (accuracy of the different weighings) as well as inaccuracies due to sample handling, which will be discussed in detail later on. The measured solubilities w_{sat} could be reproduced to better than 2% (10 replicate samples for pure substances, 3 replicate samples for select solvent concentrations for binary or ternary solvent mixtures). Solubilities $w_{sat} \leq 0.05$ mass % are within the error latitude and can therefore only be regarded as rough approximations of the true solubility values.

Results and Discussion

To test the absolute reliability of the experimental procedure, solubilities of sodium chloride in the pure solvents methanol and ethanol as well as in mixtures of methanol and cyclohexane were compared with literature data. The relative deviations $\sigma^{lit}_{w_{sat}}$ between experimental solubility data w_{sat} and literature values w^{lit}_{sat} as calculated according to

$$\sigma^{lit}_{w_{sat}} = \frac{w_{sat} - w^{lit}_{sat}}{w^{lit}_{sat}} \qquad (1)$$

amount to less than −1.5% for methanol (Stephen and Stephen, 1964; Schäfer and Lax, 1962; Zhifen et al., 1980), to less than −10% for ethanol (Stephen and Stephen, 1964), and to ≤±2.5% for methanol + cyclohexane (Zhifen et al., 1980) (see Table 2 for experimental data). The large relative deviation $\sigma^{lit}_{w_{sat}}$ for ethanol is at least partly due to deviations among literature data themselves of more than 50%.

The comparison to literature shows that in most cases the experimental solubilities presented in this publication are smaller than the corresponding literature values. This is due to a systematic error caused by small drops of the saturated solution remaining on the surface of the glass cylinder during the separation of the saturated solution from the undissolved salt. The remaining solution is evaporated during the drying process, and the originally dissolved salt is deposited on the glass surface and/or inside the glass sinter plate.

Table 2. Solubility of Sodium Chloride w_{sat} in Binary Solvent Mixtures at 298.15 K with $\tilde{w}_{2,12}$ Being the Concentration of Solvent 2 in the Salt-*free* Solvent Mixture 12

$\tilde{w}_{2,12}$/ mass %	w_{sat}/ mass %	no. of liquid phases	$\tilde{w}_{2,12}$/ mass %	w_{sat}/ mass %	no. of liquid phases
Methanol (1) + Cyclohexane (2)					
0.00	1.37	1	59.73	0.26	2
10.17	0.97	1	59.86	0.25	2
18.76	0.72	1	64.66	0.22	2
21.96	0.65	1	64.87	0.22	2
29.85	0.50	1	69.83	0.19	2
39.48	0.41	2	69.85	0.21	2
39.83	0.40	2	79.92	0.10	2
49.80	0.32	2	89.95	(0.05)	2
49.87	0.33	2	100.00	(0.001)	1
Water (1) + Benzyl Alcohol (2)					
0.00	26.38	1	89.92	2.02	2
70.00	8.77	2	93.04	0.96	2
70.02	8.76	2	94.89	0.10	2
74.98	7.14	2	94.95	0.27	2
80.00	5.46	2	94.98	0.06	2
80.03	5.55	2	95.05	(0.02)	2
85.02	3.81	2	97.01	(0.05)	
89.91	2.11	2	100	(0.01)	1
Water (1) + Cyclohexanol (2)					
0.00	26.40	1	79.98	5.61	2
2.02	25.55	1	85.03	3.53	2
3.83	25.51	1	88.22	2.52	1
20.05	21.99	2	89.92	1.89	1
50.06	14.81	2	89.96	1.78	1
66.67	9.73	2	90.12	1.74	1
70.05	8.66	2	95.01	0.08	1
75.02	7.07	2	95.03	0.10	1
79.76	5.39	2			

For calculating the magnitude of the systematic error, it was estimated that about 4% of the surface of the glass cylinder remains covered by solution droplets. The amount of dissolved salt, Δm_s, which is not taken into account for calculating the solubility, is proportional to the volume V_{ad} of the solution remaining in the cylinder (droplet volume and solution adhering to the frit) and to the solubility of the salt

$$\Delta m_s = V_{ad}\, \rho_{sat} w_{sat} = m_{ad} w_{sat} \qquad (2)$$

with ρ_{sat} being the density of the saturated solution. Exemplary, the droplet volume adhering to the cylinder surface was calculated to amount to 1.35 mL resulting in an entire adhering volume of $V_{ad} \approx 1.5$ mL. A differential weighing of the glass cylinders before and after the measurements confirmed this approximation. The true solubility value w^*_{sat} can be calculated according to

$$w^*_{sat} = \frac{m_s + \Delta m_s}{m_s + \Delta m_s + m_{LM}} \qquad (3)$$

The additional amount of salt adhering to the glass cylinder and the frit might thus cause the measured solubility w_{sat} to be smaller than the true solubility value by a maximum of 3%. A comparison of the corrected experimental solubilities calculated using eqs 2 and 3 with the corresponding literature values yields relative devia-

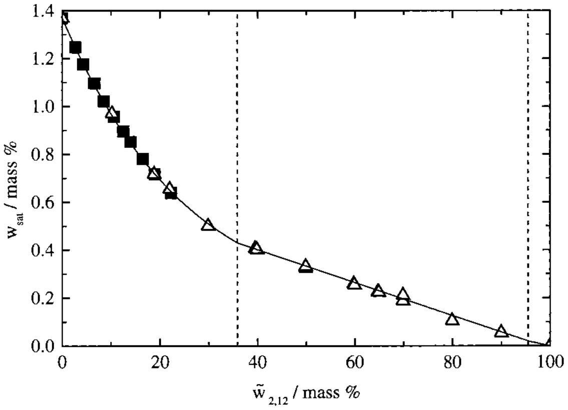

Figure 1. Solubility of NaCl (3) in methanol (1) + cyclohexane (2) at 298.15 K. △, this work; ■, Zhifen et al. (1980); —, eq 2; - - -, two-phase region (Sørensen and Arlt, 1979).

tions of less than 0.7% for methanol and of less than −7% for ethanol.

Binary Solvent Systems. The experimental solubilities w_{sat} of sodium chloride in binary solvent mixtures are reported in Table 2 as mass percentages of salt in the saturated solution. The concentration $\tilde{w}_{2,12}$ of the solvent mixtures represents the mass percentage of solvent 2 in the salt-*free* solvent mixture of solvents 1 and 2. The solubilities are not corrected for the systematic error discussed above since this correction would require the exact knowledge of the density of the saturated solution. Usually, it is the maximum solubility limit that is of interest for practical purposes so that one is on the safer side when using the uncorrected experimental solubility data, being smaller than the veritable solubilities. However, if the density of the saturated solution is known, the true solubility value can be calculated according to eqs 2 and 3.

The solubility data for the system methanol (1) + cyclohexane (2) + NaCl (3) are displayed in Figure 1. A comparison of the experimental data for this system with data taken from literature (Zhifen et al., 1980) is included in Figure 1 and confirms the reliability of the experimental method used here. In contrast to Zhifen et al. (1980) who used a titration method to determine the concentration of the saturated solution and who were thus limited to the single-phase region, the gravimetric method used here permits the determination of solubility data over the entire concentration range of the solvent mixture comprising the miscibility gap.

The solid line in Figure 1 represents the correlation of the solubility limits for sodium chloride in methanol + cyclohexane as calculated by eq 4 as a function of the solvent concentration in the salt-*free* solution

$$y = a + b_1x + b_2x^2 + b_3x^3 + b_4x^4 \qquad (4)$$

with $y = w_{sat}$/mass % and $x = \tilde{w}_{2,12}$/mass %. The dimensionless parameters a, b_1, ..., b_4 are listed in Table 3. The salt-*free* solution of methanol (1) + cyclohexane (2) is split into two liquid phases for cyclohexane concentrations between $\tilde{w}_{2,12} = 35.83$ mass % and $\tilde{w}_{2,12} = 95.46$ mass % (Sørensen and Arlt, 1979). The solubility of sodium chloride within this two-phase region can be described by a straight line (see Table 3). The standard deviation between experimental data and the solubility data as calculated with eq 4 amounts to 0.76% for the single-phase regions and to 6.66% for the two-phase region.

Table 3. Parameters for Eq 4

parameter	value single-phase regions	 two-phase region
a	1.370 52	$6.766\,11 \times 10^{-1}$
b_1	$-4.784\,55 \times 10^{-2}$	$-6.878\,40 \times 10^{-3}$
b_2	$8.404\,10 \times 10^{-4}$	
b_3	$-7.545\,78 \times 10^{-6}$	
b_4	$2.555\,81 \times 10^{-8}$	

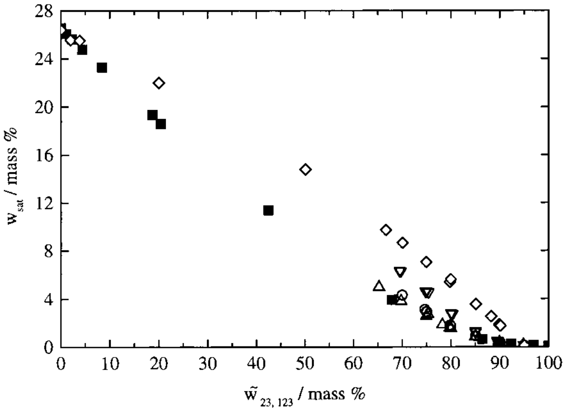

Figure 2. Solubility of NaCl (4) in water (1) + ethanol (2) + cyclohexanol (3) at 298.15 K for $\tilde{x}_{2,23}$ of ◇, 0 mol %; ▽, 61 mol %; ○, 83 mol %; △ 93 mol %; ■, 100 mol % (Stephen and Stephen, 1964).

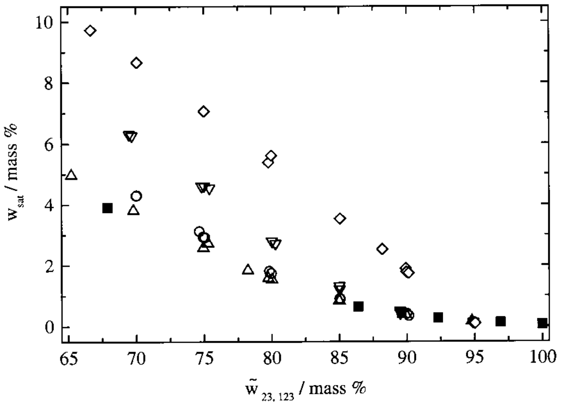

Figure 3. Solubility of NaCl (4) in water (1) + ethanol (2) + cyclohexanol (3) at 298.15 K (detailed plot of Figure 2) for $\tilde{x}_{2,23}$ of ◇, 0 mol %; ▽, 61 mol %; ○, 83 mol %; △, 93 mol %; ■, 100 mol % (Stephen and Stephen, 1964).

The measured solubilities for water (1) + (cyclohexanol or benzyl alcohol) (2) + NaCl (3) are included in Figures 2 and 4, respectively, as limiting binary solvent systems for the ternary solvent systems water (1) + (ethanol or benzyl alcohol) (2) + cyclohexanol (3).

Ternary Solvent Systems. Table 4 gives the (uncorrected) solubility data for sodium chloride in the ternary solvent mixtures water (1) + ethanol (2) + cyclohexanol (3) and water (1) + benzyl alcohol (2) + cyclohexanol (3), respectively. The salt solubility w_{sat} is again given in mass % referring to the *entire* solution, whereas the solvent concentrations $\tilde{w}_{23,123}$ and $\tilde{x}_{2,23}$ represent the mass concentration of the binary organic solvent mixture 23 made up of components 2 and 3 relative to the salt-*free* ternary solvent mixture 123 in percent and the mole concentration of component 2 (in percent) in the (salt-*free*) binary organic solvent mixture 23, respectively. The solubility data are displayed in Figures 2, 3, and 4, respectively. The solubilities of sodium chloride in the binary solvent mixtures water (1) + cyclohexanol (3) and water (1) + (ethanol or benzyl

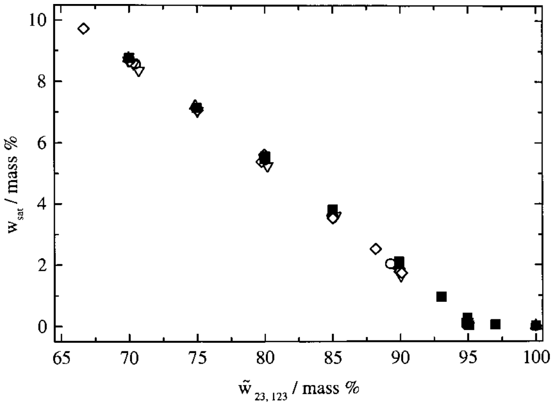

Figure 4. Solubility of NaCl (4) in water (1) + benzyl alcohol (2) + cyclohexanol (3) at 298.15 K for $\tilde{x}_{2,23}$ of ◇, 0 mol %; ▽, 22 mol %; ○, 46 mol %; △, 72 mol %; ■, 100 mol %.

Table 4. Solubility of Sodium Chloride w_{sat} in Ternary Solvent Mixtures at 298.15 K with $\tilde{w}_{23,123}$ and $\tilde{x}_{2,23}$ Being the Mass Percentage of the Binary Solvent Mixture 23 in the Salt-*free* Ternary Solvent Mixture 123 and the Mole Percentage of Component 2 in the Salt-*free* Binary Solvent Mixture 23, Respectively

$\tilde{w}_{23,123}$/ mass %	$\tilde{x}_{2,23}$/ mol %	w_{sat}/ mass %	$\tilde{w}_{23,123}$/ mass %	$\tilde{x}_{2,23}$/ mol %	w_{sat}/ mass %
Water (1) + Ethanol (2) + Cyclohexanol (3); $\tilde{x}_{2,23} \approx 61$ mol %					
69.47	62.21	6.31	80.28	60.51	2.71
69.67	61.70	6.26	85.01	61.17	1.32
74.81	61.36	4.61	85.02	61.30	1.21
74.98	61.17	4.62	89.49	61.24	0.50
75.39	60.31	4.54	89.52	61.82	0.42
80.01	61.35	2.79	94.89	62.12	(0.01)
Water (1) + Ethanol (2) + Cyclohexanol (3); $\tilde{x}_{2,23} \approx 83$ mol %					
70.00	82.55	4.29	79.97	82.51	1.74
70.03	82.53	4.30	85.03	82.52	0.91
74.65	82.50	3.12	85.06	82.52	0.90
74.93	82.76	2.94	90.00	82.54	0.41
75.06	82.57	2.92	90.14	82.34	0.34
79.83	82.32	1.81	94.97	83.23	0.11
Water (1) + Ethanol (2) + Cyclohexanol (3); $\tilde{x}_{2,23} \approx 93$ mol %					
65.22	93.42	4.97	80.02	93.39	1.53
69.79	93.25	3.81	84.97	93.42	0.84
74.95	93.43	2.58	85.01	93.39	0.83
75.29	92.69	2.72	89.91	93.26	0.38
78.23	93.41	1.84	94.79	93.57	0.16
79.75	93.50	1.58			
Water (1) + Benzyl Alcohol (2) + Cyclohexanol (3); $\tilde{x}_{2,23} \approx 22$ mol %					
69.96	22.22	8.69	80.20	21.94	5.25
70.34	21.87	8.58	85.24	21.89	3.61
70.72	23.06	8.36	90.06	22.11	1.65
75.03	22.21	7.05	94.94	22.25	0.13
Water (1) + Benzyl Alcohol (2) + Cyclohexanol (3); $\tilde{x}_{2,23} \approx 46$ mol %					
70.48	45.16	8.57	85.03	46.20	3.64
75.03	45.89	7.11	89.29	46.14	2.03
79.95	46.02	5.44	95.00	46.13	0.07
Water (1) + Benzyl Alcohol (2) + Cyclohexanol (3); $\tilde{x}_{2,23} \approx 72$ mol %					
69.97	71.87	8.75	84.99	72.00	3.71
74.86	71.99	7.21	89.90	72.01	1.98
79.95	72.06	0.54	94.98	71.97	0.12

alcohol) (2) ($\tilde{x}_{2,23} = 0$ and $\tilde{x}_{2,23} = 1$, respectively) are included to give a better overview of the dependence of the solubility on the composition of the organic solvent subsystem. Figure 3 is a detailed plot of the right-hand side of Figure 2 corresponding to that part of the solvent system which is rich in organic phase. This detail plot is included to permit a direct comparison of the solubilities of sodium chloride in the two ternary solvent mixtures.

Solubilities of sodium chloride in the ternary mixtures mentioned above were not determined over the entire concentration range from pure water (1) to the pure organic mixture (23) because it is usually the region with a low limit of salt solubility (i.e., the region rich in organic solvent or organic solvent mixture) which is of interest for most technical applications since a salt deposit inside an apparatus has to be excluded by all means. Thus, only solution concentrations of more than 65 mass % of organic mixture relative to the salt-*free* solution were considered, i.e., $0.65 \leq \tilde{w}_{23,123} \leq 1$.

While the solubility data for the system water (1) + benzyl alcohol (2) + cyclohexanol (3) + NaCl (4) do not vary significantly with the concentration $\tilde{x}_{2,23}$ of the binary organic solution of components 2 and 3 (see Figure 4), there is a definite dependence of the solubility of sodium chloride on $\tilde{x}_{2,23}$ in the system water (1) + ethanol (2) + cyclohexanol (3) + NaCl (4) (see Figure 3). Apparently, the dissolving capacity of benzyl alcohol and of cyclohexanol for sodium chloride is of the same order of magnitude owing to the somewhat similar structure of the two components. The organic components of the second solvent system, however, i.e., ethanol and cyclohexanol, show a completely different chemical structure resulting in a different dissolving capacity for different concentrations of ethanol and of cyclohexanol in the organic solution.

The ternary solvent mixtures under consideration form two liquid phases over a large part of the concentration range displayed in Figures 3 and 4, respectively. While there is hardly any difference visible in the slope of the straight lines formed by the solubility data points in this two-phase region for the system water + benzyl alcohol + cyclohexanol + NaCl, the slope for the solubility limit lines increases significantly with the concentration of cyclohexanol in the system water + ethanol + cyclohexanol + NaCl thus reducing the extension of the two-phase region toward the aqueous side of the solvent concentration.

Conclusion

When designing and operating separation plants and other chemical engineering processing units, information about the solubility limits of salts being present in most chemical processes is needed in order to perform a desired separation or to prevent an unwanted salt deposit inside an apparatus. In this work, a gravimetric procedure has been used to determine solubilities of sodium chloride in binary organic and aqueous–organic solvent mixtures as well as in ternary aqueous–organic mixtures at 298.15 K. A systematic error might cause the experimental data to be smaller than the corresponding veritable solubilities. This is, however, accepted since the determined solubilities thus represent a worst case estimate for basic engineering applications. Generally speaking, however, the procedure used for the solubility measurements in this publication is found to produce reliable experimental results.

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