Solubilities for Six Ternary Systems: $NaCl + NH_4Cl + H_2O$, $KCl + NH_4Cl + H_2O$, $NaCl + LiCl + H_2O$, $KCl + LiCl + H_2O$, $NaCl + AlCl_3 + H_2O$, and $KCl + AlCl_3 + H_2O$ at T = (298 to 333) K

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The entire phase diagrams of the ternary systems $NaCl + NH_4Cl + H_2O$, $KCl + NH_4Cl + H_2O$, $NaCl + AlCl_3 + H_2O$, and $KCl + AlCl_3 + H_2O$, as well as the solubilities of sodium and potassium chlorides in aqueous solutions of lithium chloride, were determined at T = (298 to 333) K. Additionally, the equilibrium concentrations of pure ammonium chloride, lithium chloride monohydrate salt, and aluminum chloride-6-hydrate were also measured over the same range of temperatures. The measured data were correlated as a function of temperature and content of the secondary electrolyte in the solvent by a least-squares method. The proposed empirical equations of fit allow fair agreement between calculated and experimental data, the invariant composition mixtures included, with standard deviations of fit to molality ranging from ±(0.02 to 0.05) mol·kg^{-1}. In concentrated solutions of lithium and aluminum chlorides, the equilibrium concentrations of NaCl and KCl become very small. Therefore, because of the form of the optimization criterion chosen for the fit, the relative deviations between the two sets of data increase directly with the content of the secondary electrolyte.

Introduction

Solid−liquid equilibrium data pertaining to inorganic salts in mixed-salt aqueous solutions are fundamental tools in the design and simulation of crystallization operations and in supporting mathematical frameworks developed for the thermodynamics of electrolytes. However, for many multicomponent systems the solubility data are scarce or nonexistent. When available, the large majority of the reported values concern systems at 298 K, thus being of little use for most engineering applications.

The paucity of literature data concerning the solubility of sodium and potassium chlorides in aqueous solutions of lithium chloride or aluminum chloride led us to study the solid−liquid phase diagrams of these salts in the temperature range of T = (298 to 333) K. The solubility diagrams of the ternary systems $NaCl + NH_4Cl + H_2O$ and $KCl + NH_4Cl + H_2O$ were also experimentally obtained over the entire concentration range and were compared to the available literature data. During the course of this study, the solubilities in water of NH_4Cl, $LiCl·H_2O$, and $AlCl_3·6H_2O$ were measured.

Experimental Section

Analytical-grade potassium chloride, sodium chloride, and aluminum chloride-6-hydrate were supplied by Riedel-de Haën with minimum purities of 99.5%, 99.8% and 99.5%, respectively. Ammonium chloride (99.5%+) and lithium chloride monohydrate Suprapur (99.95%) were Merck products. The silver nitrate volumetric standard 0.1025 mol·dm^{-3} solution in water, used as a titration reagent, was purchased from Aldrich. Standard stock solutions for atomic absorption spectroscopy were also supplied by Merck.

Prior to the preparation of the solutions, the chlorides of potassium and sodium were oven dried at 120 °C for 24 h. Ammonium chloride, lithium chloride monohydrate, and aluminum chloride-6-hydrate were kept under a continuous flow of nitrogen for at least 36 h. Deionized water with a specific conductivity of 1.4 μS·cm^{-1} was used.

Single-salt solutions of NaCl, KCl, and NH_4Cl in water were prepared by mass, with an uncertainty of $\pm 1 \times 10^{-2}$ g. Because of the strongly hygroscopic behavior of lithium and aluminum chlorides, the aqueous solutions of these salts were potentiometrically titrated with a standard $AgNO_3$ solution to determine the chloride content. The titrations were performed in triplicate using a Metrohm electrode (6.0450.100 Ag/0...70 °C KNO_3(sat)) and a 686 Metrohm titroprocessor coupled to a Dosimat 665 buret. The chloride ion content was obtained with an uncertainty of better than ±0.8% of the measured concentration.

Lithium and aluminum chloride solutions are irritating and corrosive to the skin and eyes, thus requiring the use of safe laboratory gear such as glasses and gloves during the experiments. Wearing a mask while handling aluminum chloride solutions is mandatory because the salt hydrolyzes to give aluminum oxychloride and hydrochloric acid. The solutions thus formed are strongly acidic, even for low salt concentrations (pH of 2.75 and 1.47, at 20 °C, for aqueous solutions with (0.375 and 1.49) mol·kg^{-1} of $AlCl_3$, respectively). Above 333 K, the release of gaseous hydrochloric acid from concentrated solutions is significant.

Apparatus and Procedures. Solubility data pertaining to the crystallization fields of NaCl, KCl, and NH_4Cl were measured at T = (298 to 333) K using the visual polythermal method of Potter and Clynne.[1] The invariant data, as well as equilibrium concentrations of lithium and aluminum chlorides in water and of $AlCl_3$ in the ternary mixtures with NaCl or KCl, were obtained by the isothermal solubility technique.

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Table 1. Solubilities of Sodium Chloride, S_{NaCl}, and Ammonium Chloride, S_{NH4Cl}, in the NaCl + NH_4Cl + Water System

T/K	S_{NaCl}/mol·kg^{-1}	T/K	S_{NaCl}/mol·kg^{-1}	T/K	S_{NH_4Cl}/mol·kg^{-1}	T/K	S_{NH_4Cl}/mol·kg^{-1}
$m_{NH_4Cl} = 0.9346$ mol·kg^{-1}		$m_{NH_4Cl} = 3.7390$ mol·kg^{-1}		$m_{NaCl} = 0.4277$ mol·kg^{-1}		$m_{NaCl} = 2.5660$ mol·kg^{-1}	
297.5	5.7499	297.4	4.6257	296.9	6.8847	299.4	5.5967
302.0	5.7766	304.3	4.6669	302.4	7.3404	302.9	5.8736
309.1	5.8248	310.8	4.7092	308.3	7.7469	308.7	6.2632
315.0	5.8505	317.2	4.7660	312.9	8.1279	313.0	6.6076
322.9	5.9642	325.3	4.8825	318.1	8.5773	316.4	6.8809
329.3	6.0024	333.6	4.9805	324.3	9.0787	323.3	7.4113
332.3	6.0243	$m_{NH_4Cl} = 4.6749$ mol·kg^{-1}		332.4	9.7972	328.7	7.8215
$m_{NH_4Cl} = 1.8697$ mol·kg^{-1}		310.4	4.3868	$m_{NaCl} = 0.8556$ mol·kg^{-1}		332.4	8.1333
295.5	5.3490	315.6	4.4265	293.2	6.3285	$m_{NaCl} = 3.4224$ mol·kg^{-1}	
300.2	5.3728	324.0	4.5487	297.6	6.6476	299.6	5.0694
304.7	5.4015	334.1	4.6323	304.2	7.1458	306.9	5.5586
311.7	5.4306	$m_{NH_4Cl} = 5.6068$ mol·kg^{-1}		309.0	7.5412	314.4	6.1071
314.4	5.5124	315.8	4.1521	316.4	8.1292	327.0	7.0671
321.7	5.5507	321.4	4.2051	323.1	8.6814	334.3	7.6268
326.8	5.5831	327.1	4.3085	329.6	9.1823	$m_{NaCl} = 3.8154$ mol·kg^{-1}	
333.1	5.6322	332.7	4.3254	332.7	9.4567	297.6	4.7001
$m_{NH_4Cl} = 2.8038$ mol·kg^{-1}		$m_{NH_4Cl} = 6.5423$ mol·kg^{-1}		$m_{NaCl} = 1.7109$ mol·kg^{-1}		303.9	5.1011
291.5	4.9531	326.2	3.9579	297.5	6.0686	311.3	5.6177
298.7	4.9825	331.4	4.0275	302.6	6.4279	317.8	6.1004
305.6	5.0238	335.6	4.0678	307.3	6.7955	331.5	7.1196
312.2	5.0684			312.6	7.1862		
317.9	5.1690			322.8	8.0166		
322.2	5.2103			327.8	8.3862		
328.1	5.2570			331.7	8.7414		
332.3	5.3073						

Table 2. Solubilities of Potassium Chloride, S_{KCl}, and Ammonium Chloride, S_{NH_4Cl}, in the KCl + NH_4Cl + Water System

T/K	S_{KCl}/mol·kg^{-1}	T/K	S_{KCl}/mol·kg^{-1}	T/K	S_{NH_4Cl}/mol·kg^{-1}	T/K	S_{NH_4Cl}/mol·kg^{-1}
$m_{NH_4Cl} = 0.9348$ mol·kg^{-1}		$m_{NH_4Cl} = 2.8058$ mol·kg^{-1}		$m_{KCl} = 0$ mol·kg^{-1}		$m_{KCl} = 1.0075$ mol·kg^{-1}	
296.8	4.3190	317.8	4.1483	293.4	6.9892	302.5	7.0475
300.6	4.3804	326.6	4.4936	297.8	7.3294	309.8	7.6012
304.7	4.5432	333.5	4.7589	303.2	7.7347	320.0	8.4156
310.4	4.7676	$m_{NH_4Cl} = 4.6749$ mol·kg^{-1}		307.6	8.0965	325.0	8.8645
318.2	5.0708	298.4	2.6741	313.3	8.5132	332.2	9.4698
324.5	5.3188	303.4	2.8415	318.8	8.9720	$m_{KCl} = 1.3427$ mol·kg^{-1}	
326.0	5.3763	311.1	3.0975	323.7	9.4391	298.8	6.5895
328.6	5.4689	313.6	3.2290	329.1	9.8405	303.4	6.9349
$m_{NH_4Cl} = 1.8704$ mol·kg^{-1}		325.4	3.6304	333.4	10.2266	310.9	7.4937
298.5	3.8419	334.0	3.9291	340.2	10.7710	315.4	7.7777
304.4	4.0586	$m_{NH_4Cl} = 6.0744$ mol·kg^{-1}		$m_{KCl} = 0.5365$ mol·kg^{-1}		320.7	8.2842
317.3	4.5711	304.6	2.3228	296.5	6.8582	328.4	8.9215
328.2	4.9869	310.2	2.5174	301.9	7.2840	332.3	9.2733
335.1	5.2466	314.1	2.6793	307.0	7.6556	$m_{KCl} = 2.1440$ mol·kg^{-1}	
$m_{NH_4Cl} = 2.8058$ mol·kg^{-1}		320.0	2.8573	317.8	8.5390	301.7	6.1913
297.4	3.4264	324.5	3.0849	322.6	8.9346	306.6	6.5592
300.6	3.5405	328.2	3.1766	323.9	9.0537	314.9	7.2697
305.7	3.6975	334.9	3.4402	331.9	9.7370	318.0	7.4995
311.4	3.9010			$m_{KCl} = 1.0075$ mol·kg^{-1}		324.2	8.0202
				297.7	6.5678	331.5	8.7580

The solubilities were measured in a tightly sealed 100-mL glass cell equipped with a Teflon-coated magnetic stirrer and a sampling port with a septum, allowing the insertion of a hypodermic syringe when necessary. The flask was loaded with weighed amounts of salt and water or solution with a known content of the secondary electrolyte, leaving a gas-phase volume not larger than (3 to 5) mL. The cell was then immersed in a thermostated bath (Haake C-F3 or Grant W6) controlled to ±0.1 K. According to the visual polythermal method, the temperature was raised by increments that were made progressively smaller as the number and size of the existing crystals decreased. Near the equilibrium temperature, at least 1 h elapsed between consecutive increments of 0.1 K. When the last crystal was dissolved, it was assumed that equilibrium conditions corresponding to the bulk composition of the system had been reached.

Temperatures were measured in the thermostated fluid and read with an uncertainty of ±0.03 K, with a set of Landsberger glass precision thermometers {(+17 to +35) °C, (+34 to +52) °C, and (+51 to +68) °C} certified by Glasmessgeräte Darmstadt and calibrated to the ITS-90 scale. At no time did the temperature difference outside and inside the solubility cell exceed ±0.05 K after 20 min of equilibration.

The saturation temperatures reported here are the average values of at least two identical readings on the same sample, with an uncertainty of better than ±0.1 K. The equilibrium concentrations of NaCl, KCl, and NH_4Cl were calculated from the masses of solid salt and solvent loaded into the cell (uncertainty of $\pm 1 \times 10^{-4}$ g) and from the known content of the secondary electrolyte in the solvent.

The determination of the solubilities of the lithium and aluminum hydrate chlorides was carried out in the previously described cell by equilibrating the solid salt in water (or in solutions with NaCl or KCl) at constant temperature. The contents of the cell were stirred for 6 h, followed by a settling period of about 3 h. At the end of the experiment, the saturated solution was sampled for analysis. The invariant points' determination was also carried out according to the isothermal technique. In this case, a small

Table 3. Experimental Invariant Points' Compositions in NaCl + NH_4Cl + Water and KCl + NH_4Cl + Water Systems

	NaCl + NH_4Cl + water		KCl + NH_4Cl + water	
T/K	m_{NH_4Cl}/mol·kg^{-1}	m_{NaCl}/mol·kg^{-1}	m_{NH_4Cl}/mol·kg^{-1}	m_{KCl}/mol·kg^{-1}
298.2	4.35	4.3	5.75	2.23
303.2			6.29	2.25
313.1	5.41	4.1	6.82	2.32
323.0			7.81	2.40
332.9	7.09	3.9	8.82	2.43

Table 4. Solubilities of $LiCl{\cdot}H_2O$, S_{LiCl}, in Water

T/K	S_{LiCl}/mol·kg^{-1}
296.7	19.7
298.4	19.9
303.1	20.0
308.0	20.7
313.3	21.1
318.0	21.4
323.2	22.1
328.2	22.5
330.6	23.1
334.5	23.5

Table 5. Solubilities of Potassium Chloride, S_{KCl}, in the KCl + LiCl + Water System for Different Temperatures and Contents of LiCl

T/K	S_{KCl}/mol·kg^{-1}	T/K	S_{KCl}/mol·kg^{-1}	T/K	S_{KCl}/mol·kg^{-1}
m_{LiCl} = 1.00 mol·kg^{-1}		m_{LiCl} = 9.32 mol·kg^{-1}		m_{LiCl} = 15.5 mol·kg^{-1}	
298.3	3.982	296.9	0.650	301.2	0.555
302.6	4.158	301.4	0.718	308.4	0.698
308.2	4.367	310.1	0.823	317.4	0.862
312.3	4.538	315.1	0.931	324.7	0.955
316.8	4.712	322.4	1.063	326.9	1.021
322.2	4.874	327.0	1.168	329.8	1.047
m_{LiCl} = 1.97 mol·kg^{-1}		335.5	1.368	m_{LiCl} = 16.8 mol·kg^{-1}	
293.0	3.122	m_{LiCl} = 10.61 mol·kg^{-1}		294.0	0.539
298.4	3.346	298.8	0.555	305.0	0.681
303.7	3.528	303.5	0.620	308.9	0.735
308.6	3.682	308.5	0.736	314.1	0.830
313.7	3.886	312.5	0.770	323.7	0.952
318.3	4.018	318.7	0.917	332.8	1.132
323.5	4.211	323.5	0.954	m_{LiCl} = 17.5 mol·kg^{-1}	
332.9	4.583	328.6	1.080	293.5	0.560
m_{LiCl} = 3.93 mol·kg^{-1}		m_{LiCl} = 12.7 mol·kg^{-1}		297.0	0.606
297.2	2.089	295.0	0.477	299.8	0.672
301.4	2.206	298.5	0.489	301.3	0.676
308.2	2.417	300.0	0.534	302.5	0.694
313.5	2.601	303.2	0.589	307.8	0.805
318.0	2.748	318.0	0.786	313.5	0.872
324.1	2.940	324.0	0.930	316.0	0.914
m_{LiCl} = 5.94 mol·kg^{-1}		327.2	0.946	317.4	0.939
296.4	1.286	332.1	1.074	323.7	1.041
304.5	1.448	m_{LiCl} = 13.1 mol·kg^{-1}		326.7	1.089
308.6	1.522	294.7	0.475	332.8	1.209
313.7	1.660	302.5	0.564	330.1	1.144
318.6	1.788	312.3	0.670	m_{LiCl} = 18.8 mol·kg^{-1}	
323.1	1.881	319.5	0.781	298.5	0.672
329.1	2.029	324.5	0.874	302.1	0.739
333.9	2.163	331.9	1.019	309.3	0.874
m_{LiCl} = 7.05 mol·kg^{-1}		m_{LiCl} = 14.1 mol·kg^{-1}		316.4	1.006
297.6	0.994	300.0	0.516	324.0	1.153
303.3	1.110	323.3	0.855	332.2	1.275
308.2	1.190	325.9	0.907		
312.7	1.312	329.4	0.961		
324.1	1.575				
332.8	1.745				

excess of both solid salts was equilibrated in water for 24 h at constant temperature, and a settling period of about 6 h was allowed, prior to sampling.

The equilibrium concentrations of the aluminum and lithium chlorides in water were obtained titrimetrically to ±0.8%. For this purpose, two liquid samples of about 4 mL were collected at the end of each experiment and quickly injected into capped vials containing a known mass of distilled water. The sampling syringe, equipped with a 0.45-μm filter, was previously heated at a temperature slightly above the equilibrium value to prevent precipitation. Two aliquots of the diluted solutions were titrated with a 0.1025 mol·dm^{-3} $AgNO_3$ standard solution, and the equilibrium concentrations were calculated from the chloride content and from the masses of the diluted solution and the sample collected. The reported solubilities are the mean values of duplicate analyses on each of the two samples.

The contents of sodium and potassium in the cosaturated solutions and in the crystallization field of aluminum chloride hexahydrate were obtained by atomic absorption spectroscopy in a Perkin-Elmer model A Analyst 200 instrument at wavelengths of (769.9 and 330.2) nm, respectively. The concentration of the sodium standards ranged from (0 to 80) mg·dm^{-3} in a 0.1% volume KCl matrix, whereas the calibration line for potassium was established over the concentration range of (0 to 20) mg·dm^{-3} in 0.1% volume CsCl. To compensate for matrix interferences, appropriate amounts of the secondary electrolyte existing in the samples were added to blanks and standards. The reproducibility of triplicate determinations was better than (±0.4 and ±1.5)% for potassium and sodium, respectively. The uncertainty in the contents of the corresponding chloride salts, evaluated from measurements on the standard solutions and from the uncertainty of the experimental procedures, was (±1 and ±5.2)%. The concentrations of ammonium, lithium, and aluminum were determined by difference from the total amount of chloride ion obtained titrimetrically, with the respective maximum uncertainties being (±0.09, ±0.3, and ±0.04) mol·kg^{-1}.

Results and Data Treatment

The equilibrium data measured at T = (298 to 333) K over the entire range of salt composition in aqueous mixtures of NaCl + NH_4Cl and KCl + NH_4Cl are reported in Tables 1 and 2, respectively, whereas the invariant points' compositions are tabulated in Table 3. For all fields of both solubility diagrams, the invariant-composition mixtures excluded, the uncertainty of the saturation molalities is better than ±0.0007 mol·kg^{-1}.

Table 4 reports the solubilities of lithium chloride in water, as an anhydrous salt, at T = (294 to 334) K with an estimated uncertainty of ±0.3 mol·kg^{-1}. The tabulated values agree to ±0.25% with the data of Clynne and Potter[2] and are well correlated by the second-order polynomial function of temperature proposed by Monnin et al.,[3] with the scatter of the experimental data around the calculated values (±0.1 mol·kg^{-1}) being lower than the measurements' uncertainty. The equilibrium data pertaining to KCl and NaCl in aqueous solutions of LiCl are tabulated in Tables 5 and 6, respectively, with a maximum uncertainty of ±0.004 mol·kg^{-1}. For the invariant points data, listed in Table 7, the estimated uncertainties in composition were (±0.006, ±0.02, and ±0.3) mol·kg^{-1}, respectively, for NaCl, KCl, and LiCl. Independent of temperature, the equilibrium molalities of lithium chloride in pure water and in the double saturated solutions with sodium or potassium chloride were nearly identical, with the deviations always being lower than the experimental uncertainty in the salt concentration. Therefore, for both ternary systems the crystallization field of the lithium salt was not investigated.

The equilibrium temperatures and concentrations measured for potassium and sodium chlorides in aqueous

Table 6. Solubilities of Sodium Chloride, S_{NaCl}, in the NaCl + LiCl + Water System for Different Temperatures and Contents of LiCl

T/K	S_{NaCl}/ mol·kg^{-1}	T/K	S_{NaCl}/ mol·kg^{-1}	T/K	S_{NaCl}/ mol·kg^{-1}
m_{LiCl} = 1.09 mol·kg^{-1}		m_{LiCl} = 5.80 mol·kg^{-1}		m_{LiCl} = 12.7 mol·kg^{-1}	
293.1	5.151	293.8	1.372	295.7	0.086
300.6	5.182	298.0	1.398	303.7	0.109
308.0	5.262	303.1	1.448	319.6	0.154
318.7	5.324	308.0	1.515	m_{LiCl} = 14.2 mol·kg^{-1}	
323.6	5.354	318.7	1.599	299.1	0.059
332.4	5.416	323.6	1.650	304.7	0.086
m_{LiCl} = 1.97 mol·kg^{-1}		328.0	1.694	314.3	0.097
293.8	4.239	332.6	1.746	322.3	0.112
297.8	4.286	m_{LiCl} = 9.67 mol·kg^{-1}		331.2	0.145
303.4	4.329	297.6	0.342	337.1	0.168
309.4	4.375	306.3	0.386	m_{LiCl} = 16.6 mol·kg^{-1}	
314.6	4.430	315.8	0.428	305.5	0.047
317.1	4.447	323.6	0.501	312.1	0.052
318.0	4.452	332.8	0.532	316.4	0.071
322.7	4.501	m_{LiCl} = 10.61 mol·kg^{-1}		m_{LiCl} = 17.5 mol·kg^{-1}	
327.2	4.492	298.5	0.239	299.8	0.043
328.8	4.546	306.0	0.250	312.0	0.052
333.3	4.596	314.5	0.298	320.7	0.086
m_{LiCl} = 3.91 mol·kg^{-1}		319.2	0.328	326.9	0.110
294.8	2.546	323.4	0.319	333.6	0.135
300.0	2.623	327.9	0.335	m_{LiCl} = 19.1 mol·kg^{-1}	
308.3	2.694	333.2	0.386	297.8	0.033
319.7	2.807	m_{LiCl} = 11.75 mol·kg^{-1}		304.1	0.045
326.1	2.862	298.8	0.152	311.8	0.057
334.4	2.952	306.4	0.180	317.3	0.068
341.0	3.040	314.2	0.207	332.5	0.116
		320.5	0.231		
		327.6	0.256		
		332.8	0.283		

Table 7. Experimental Invariant Points' Compositions in the KCl + LiCl + Water and NaCl + LiCl + Water Systems

	KCl + LiCl + water		NaCl + LiCl + water	
T/K	m_{LiCl}/ mol·kg^{-1}	m_{KCl}/ mol·kg^{-1}	m_{LiCl}/ mol·kg^{-1}	m_{NaCl}/ mol·kg^{-1}
298.2	19.7	0.87	19.8	0.034
303.2	20.1	0.98		
303.9			20.5	0.043
313.1	21.0	1.22	21.1	0.058
323.1	21.9	1.42	22.0	0.081
333.0	23.2	1.72	23.7	0.110

Table 8. Solubilities of Potassium Chloride, S_{KCl}, in Aqueous Solutions of $AlCl_3$

T/K	S_{KCl}/ mol·kg^{-1}	T/K	S_{KCl}/ mol·kg^{-1}	T/K	S_{KCl}/ mol·kg^{-1}
m_{AlCl_3} = 0.375 mol·kg^{-1}		m_{AlCl_3} = 1.49 mol·kg^{-1}		m_{AlCl_3} = 2.70 mol·kg^{-1}	
298.5	3.930	303.2	1.541	308.6	0.709
304.9	4.057	312.5	1.809	317.7	0.864
311.1	4.284	m_{AlCl_3} = 1.88 mol·kg^{-1}		329.5	1.072
320.3	4.642	297.6	0.704	m_{AlCl_3} = 2.71 mol·kg^{-1}	
324.8	4.784	299.6	0.797	297.3	0.564
335.2	5.093	304.2	0.919	306.7	0.693
338.3	5.227	305.1	0.934	320.3	0.911
m_{AlCl_3} = 0.749 mol·kg^{-1}		311.0	1.131	325.8	1.003
298.9	3.032	312.9	1.163	335.0	1.183
306.6	3.208	322.0	1.468	m_{AlCl_3} = 2.96 mol·kg^{-1}	
319.0	3.629	325.3	1.615	302.1	0.564
326.7	3.897	330.8	1.721	322.8	0.808
334.6	4.180	334.7	1.866	335.2	0.999
341.1	4.416	337.8	1.978	m_{AlCl_3} = 2.99 mol·kg^{-1}	
m_{AlCl_3} = 1.13 mol·kg^{-1}		m_{AlCl_3} = 2.14 mol·kg^{-1}		301.3	0.553
297.5	2.116	303.9	0.819	306.8	0.612
305.0	2.305	320.4	1.160	311.0	0.680
312.4	2.586	325.2	1.254	317.8	0.759
316.8	2.736	329.0	1.360	330.9	0.947
323.5	2.940	m_{AlCl_3} = 2.24 mol·kg^{-1}		336.0	1.034
331.7	3.246	298.1	0.671	m_{AlCl_3} = 3.13 mol·kg^{-1}	
m_{AlCl_3} = 1.39 mol·kg^{-1}		301.0	0.737	309.7	0.567
296.2	1.502	308.4	0.872	311.8	0.571
299.0	1.561	315.4	1.008	316.8	0.638
306.2	1.745	326.4	1.220	319.8	0.705
316.3	2.123	m_{AlCl_3} = 2.53 mol·kg^{-1}		327.4	0.805
320.8	2.254	303.1	0.712	336.5	1.011
329.6	2.555	312.7	0.859		
		318.2	0.958		
		327.6	1.157		

Table 9. Solubilities of Sodium Chloride, S_{NaCl}, in Aqueous Solutions of $AlCl_3$

T/K	S_{NaCl}/ mol·kg^{-1}	T/K	S_{NaCl}/ mol·kg^{-1}	T/K	S_{NaCl}/ mol·kg^{-1}
m_{AlCl_3} = 0.373 mol·kg^{-1}		m_{AlCl_3} = 1.13 mol·kg^{-1}		m_{AlCl_3} = 1.89 mol·kg^{-1}	
299.2	5.027	298.7	2.885	300.1	1.163
301.3	5.045	300.7	2.923	310.3	1.285
306.7	5.084	304.6	2.938	317.2	1.332
312.5	5.120	322.3	3.114	319.2	1.366
330.4	5.252	326.5	3.163	326.3	1.430
m_{AlCl_3} = 0.555 mol·kg^{-1}		329.5	3.168	m_{AlCl_3} = 2.25 mol·kg^{-1}	
298.0	4.474	335.0	3.249	296.2	0.733
305.6	4.530	m_{AlCl_3} = 1.14 mol·kg^{-1}		301.5	0.803
311.6	4.597	302.0	2.903	309.8	0.866
314.8	4.602	307.5	2.946	316.4	0.922
323.2	4.680	314.6	3.018	325.8	0.996
330.8	4.733	m_{AlCl_3} = 1.51 mol·kg^{-1}		m_{AlCl_3} = 2.79 mol·kg^{-1}	
332.6	4.754	296.9	1.959	300.8	0.306
m_{AlCl_3} = 0.750 mol·kg^{-1}		307.9	2.054	304.8	0.343
299.0	3.912	313.3	2.117	310.1	0.372
306.5	3.984	319.1	2.179	321.5	0.451
311.3	4.016	323.2	2.245	327.9	0.493
316.7	4.063	328.9	2.297	333.9	0.510
320.2	4.104	336.1	2.355	m_{AlCl_3} = 2.97 mol·kg^{-1}	
326.0	4.151	m_{AlCl_3} = 1.88 mol·kg^{-1}		299.5	0.212
330.4	4.192	295.1	1.135	306.7	0.282
m_{AlCl_3} = 0.984 mol·kg^{-1}		297.8	1.158	313.9	0.312
299.0	3.292	307.9	1.284	320.0	0.342
303.7	3.329	316.4	1.369	325.1	0.370
310.7	3.389	325.6	1.457	332.5	0.408
316.7	3.434	332.8	1.544	m_{AlCl_3} = 3.28 mol·kg^{-1}	
321.8	3.488			319.5	0.240
326.0	3.528			333.5	0.297

solutions with $AlCl_3$ are presented in Tables 8 and 9, respectively, at T = (293 to 333) K and up to near the double saturation points. The maximum uncertainty of the saturation concentrations of KCl and NaCl in those systems was ±0.003 mol·kg^{-1}. The solubilities of aluminum chloride in water and in aqueous systems with KCl and NaCl are given in Table 10, as an anhydrous salt, to ±0.03 mol·kg^{-1}. Data concerning the invariant composition mixtures are tabulated in Table 11, with estimated uncertainties in composition up to (±0.015, ±0.01, and ±0.04) mol·kg^{-1}, respectively for NaCl, KCl, and $AlCl_3$. The solubility of the hexahydrate aluminum chloride in water increases very slightly with temperature, and this trend becomes even more attenuated when the data are expressed as the anhydrous salt's molality because of the large number of hydration water molecules. The measured values were, therefore, correlated with temperature by means of a simple linear function, listed in Table 12, to within ±0.1%, which is less than the experimental uncertainty. Two single values found in the literature for the salt solubility in water, at T = (293[4] and 298[5]) K, are about 2% higher than the corresponding calculated values.

Solubilities on the molality scale measured in the ternary systems, S_{MCl}/mol·kg^{-1}, were correlated with the temperature, T/K, and the molality of the admixture, m_{NCl}, by empirical equations of the general form

$$S_{MCl} = S^0_{MCl}\, G(m_{NCl}, T) \qquad (1)$$

S^0_{MCl}, the salts' equilibrium molality in water obtained

Table 10. Solubilities of $AlCl_3 \cdot 6\ H_2O$, S_{AlCl3}, in Water and in Aqueous Solutions with KCl and NaCl

$AlCl_3$ + water		KCl + $AlCl_3$ + water			NaCl + $AlCl_3$ + water		
T/K	S_{AlCl_3}/mol·kg^{-1}	T/K	m_{KCl}/mol·kg^{-1}	S_{AlCl_3}/mol·kg^{-1}	T/K	m_{NaCl}/mol·kg^{-1}	S_{AlCl_3}/mol·kg^{-1}
298.3	3.39_5	298.2	0.191	3.33	298.1	0.086	3.28
303.2	3.40_0	298.1	0.256	3.25	298.1	0.092	3.30
308.1	3.40_6	297.8	0.393	3.23	298.2	0.138	3.26
313.1	3.41_5	298.0	0.475	3.20	303.2	0.092	3.31
317.0	3.41_7	303.2	0.190	3.38	303.5	0.137	3.29
318.4	3.42_5	303.3	0.255	3.36	310.9	0.169	3.31
323.2	3.42_7	304.8	0.472	3.29	311.3	0.19	3.30
325.7	3.43_1	323.2	0.190	3.40	313.2	0.085	3.36
333.2	3.44	323.2	0.253	3.39	313.3	0.091	3.36
338.1	3.45	323.3	0.466	3.31	313.1	0.136	3.33
		323.1	0.653	3.21	323.2	0.084	3.39
		333.1	0.189	3.43	323.2	0.19	3.34
		333.4	0.384	3.40	322.9	0.21	3.31
		333.3	0.461	3.38	333.4	0.084	3.43
		332.8	0.797	3.28	333.1	0.134	3.44
		336.5	0.914	3.23	333.2	0.23	3.41

Table 11. Experimental Invariant Points' Compositions in KCl+$AlCl_3$+Water and NaCl+$AlCl_3$+Water Systems

	KCl + $AlCl_3$ + water		NaCl + $AlCl_3$ + water	
T/K	m_{AlCl_3}/ mol·kg^{-1}	m_{KCl}/ mol·kg^{-1}	m_{AlCl_3}/ mol·kg^{-1}	m_{NaCl}/ mol·kg^{-1}
298.1	3.12	0.566	3.24	0.17
303.4	3.12	0.563	3.28	0.19
313.2	3.13	0.592	3.33	0.21
323.1	3.14	0.751	3.30	0.23
333.3	3.17	0.96		
333.9			3.40	0.29

Table 12. Solubility Equations for NaCl, KCl, NH_4Cl and $AlCl_3 \cdot 6\ H_2O$ in Water

	S^0_{MCl}/mol·kg^{-1}	rmsd's/ mol·kg^{-1}
NaCl[6]	$7.78461 - 0.01566(T/K) + 3.400 \times 10^{-5}(T/K)^2$	±0.003
NH_4Cl[a]	$-6.71113 + 0.01682(T/K) + 1.018 \times 10^{-4}(T/K)^2$	±0.02
KCl[6]	$-11.56851 + 0.06924(T/K) - 4.835 \times 10^{-5}(T/K)^2$	±0.004
$AlCl_3 \cdot 6H_2O$[a]	$2.96680 + 1.428 \times 10^{-3}(T/K)$	±0.002

[a] This work.

Table 13. Regression Coefficients for the Solubility Equation (Eq 3) and rmsd's

	NaCl + NH_4Cl		KCl + NH_4Cl	
	NaCl	NH_4Cl	KCl	NH_4Cl
A_1	−0.14846	−0.26088	−0.24971	−0.36149
A_2	6.563×10^{-4}		2.332×10^{-3}	
A_3	2.661×10^{-4}	5.685×10^{-4}	4.839×10^{-4}	9.033×10^{-4}
A_4		-2.839×10^{-5}		
rmsd/ mol·kg^{-1}	±0.03	±0.02	±0.03	±0.05

from the literature[6] or measured in this work, was described as a function of temperature by simple polynomial equations listed in Table 12. For each system, the empirical constants of the auxiliary function $G(m_{NCl}, T)$ were determined from a least-squares fit of the selected equation to the experimental data. The goodness of the fit was assessed in terms of the root-mean-square deviation in salt content, rmsd, calculated as

$$\text{rmsd} = \sqrt{\frac{\sum_{j=1}^{N}(S_{\text{calcd}} - S_{\text{exptl}})^2}{(N - p - 1)}} \qquad (2)$$

where N and p are, respectively, the number of solubility determinations and fitting parameters.

The salts solubilities in the ternary systems NaCl + NH_4Cl and KCl + NH_4Cl, are well described by substituting the following auxiliary function

$$G(m_{\text{NCl}}, T) = [1 + A_1 m_{\text{NCl}} + A_2 {m_{\text{NCl}}}^2 + (A_3 m_{\text{NCl}} + A_4 {m_{\text{NCl}}}^{0.25}) \times (T/\text{K})] \qquad (3)$$

into eq 1. The fitting coefficients for eq 3 are presented in Table 13, together with the root-mean-square deviations in salt content. For both systems, the relative deviations between calculated and experimental solubilities are always lower than 2% mass of salt, as shown in Figures 1 and 2. For the NaCl + NH_4Cl + H_2O system, the proposed empirical equations reproduce within ±2% mass of salt most of the published data,[7–9] as illustrated in Figure 3 where some literature values are plotted along the isotherms calculated at T = (293, 308, and 323) K. In Figure 4, the salts' solubilities in the KCl + NH_4Cl + H_2O system at T = (298, 313, and 323) K were also compared with published data.[8,10] The agreement between the calculated and older literature values[7,8] depends on the data set of reference, but the entire array of data pertaining to NH_4Cl and KCl at T = (293 to 338) K is correlated with a standard deviation of fit of ±0.15 mol·kg^{-1}. The data of Zhang et al.[10] is reproduced to within ±2.5% mass of salt, when the reported values at T = (298, 313, and 323) K, taken from an older source,[8] are discarded.

The solubilities of potassium and sodium chlorides in the presence of LiCl are appropriately correlated for most of the phase diagrams by combining eq 1 with an

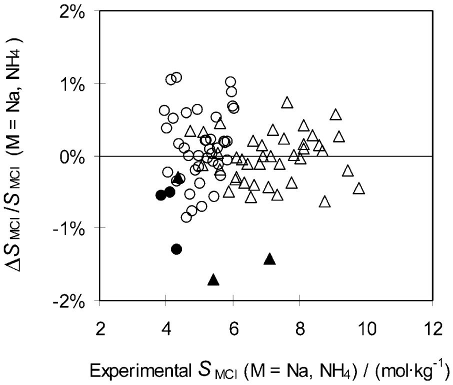

Figure 1. Relative deviations between experimental and calculated solubilities (mol·kg^{-1}) in the NaCl + NH_4Cl + H_2O system: ○, NaCl field; △, NH_4Cl field. Invariant points: ●, NaCl; ▲, NH_4Cl.

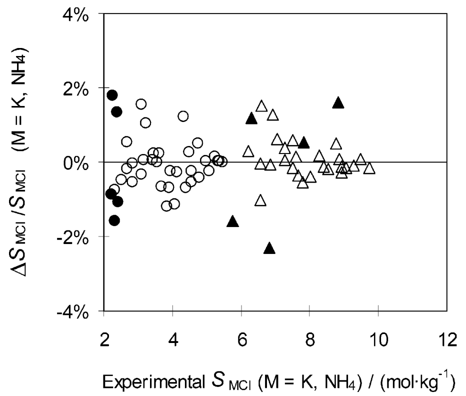

Figure 2. Relative deviations between experimental and calculated solubilities (mol·kg^{-1}) in the $KCl + NH_4Cl + H_2O$ system: ○, KCl field; △, NH_4Cl field. Invariant points: ●, KCl; ▲, NH_4Cl.

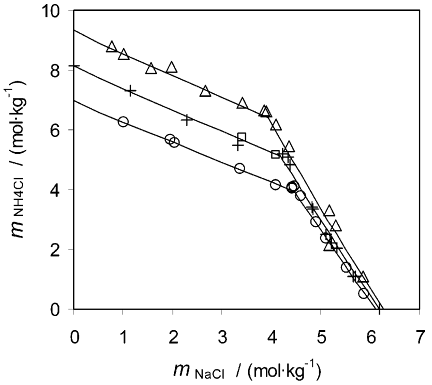

Figure 3. Literature (symbols) and calculated (lines) isotherms at T = (293, 308, and 323) K in the $NaCl + NH_4Cl + H_2O$ system. 293 K: ○, Stephen et al.[8] 308 K: □, Linke and Seidell;[7] +, Bing-Ling.[9] 323 K: △, Stephen et al.[8]

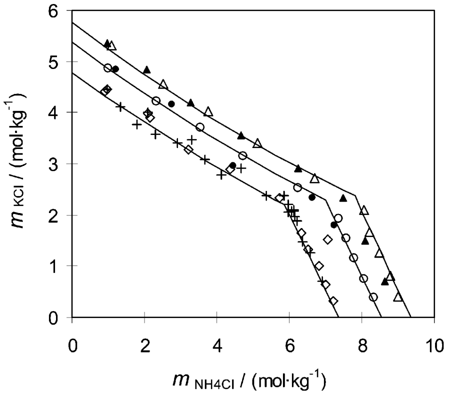

Figure 4. Literature (symbols) and calculated (lines) isotherms at T = (298, 313, and 323) K in the $KCl + NH_4Cl + H_2O$ system. 298 K: +, Stephen et al.;[8] ◇, Zhang et al.[10] 313 K: ●, Stephen et al.;[8] ○, Zhang et al.[10] 323 K: ▲, Stephen et al.;[8] △, Zhang et al.[10]

auxiliary function of the form

$$G(m_{NCl}, T) = \frac{1 + \sum_{j=1}^{2} A_j m_{NCl}^{j} + A_3 m_{NCl}(T/K)}{1 + \sum_{j=1}^{3} B_j m_{NCl}^{j}} \qquad (4)$$

For both ternary systems, the adjustable parameters and the root-mean-square deviations of fit are given in Table 14. Despite the good overall agreement between experimental and calculated values, the relative deviations of the two sets of data increase directly with the content of LiCl in the solution, as illustrated in Figure 5. (For the sake of clarity, less than half of the measured data were included here.) Near the double saturation, these deviations can be as high as (±13 and ±30)% mass of salt, respectively, in the $KCl + LiCl + H_2O$ and $NaCl + LiCl + H_2O$ systems. The contents of KCl in the invariant composition ternary mixtures are also predicted by excess.

Table 14. Regression Coefficients for the Solubility Equation (Eq 4) and rmsd's

	KCl + LiCl	NaCl + LiCl	KCl + $AlCl_3$	NaCl + $AlCl_3$
	KCl	NaCl	KCl	NaCl
A_1	−0.27199	−0.22836	−1.39927	−0.79502
A_2	6.124×10^{-3}	3.439×10^{-3}	0.17042	5.697×10^{-2}
A_3	4.633×10^{-4}	3.780×10^{-4}	2.311×10^{-3}	1.129×10^{-3}
B_1	1.646×10^{-2}	2.787×10^{-2}	-8.418×10^{-2}	8.250×10^{-2}
B_2	1.277×10^{-2}	1.407×10^{-2}	−0.16156	-6.834×10^{-2}
B_3	-2.190×10^{-4}	1.445×10^{-3}	0.17538	0.11925
rmsd/ mol·kg^{-1}	±0.04	±0.02	±0.05	±0.03

The calculated isotherms at T = (298 and 323) K for the $KCl + LiCl + H_2O$ system, plotted in Figure 6, show a large crystallization area for potassium chloride with a slight salting-in effect for contents of LiCl higher than 15 mol·kg^{-1}. This unexpected solubility trend was checked by different operators to exclude personal or experimental errors. The experimental values reported by Akopov,[11] at 298 K, were also included in the same plot. Despite notable agreement between the two sets of data in the KCl field up to the invariant point, the published solubilities of

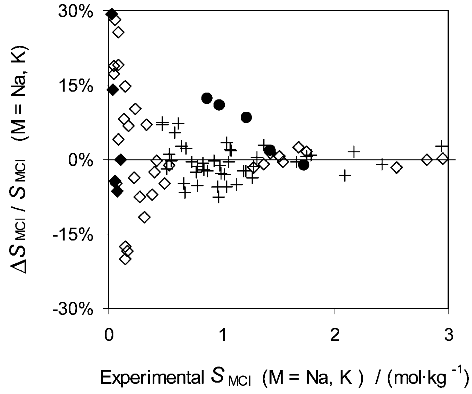

Figure 5. Relative deviations between experimental and calculated solubilities (mol·kg^{-1}) of sodium chloride and of potassium chloride in aqueous solutions with LiCl. +, KCl; ◇, NaCl. Invariant points: ●, KCl; ◆, NaCl.

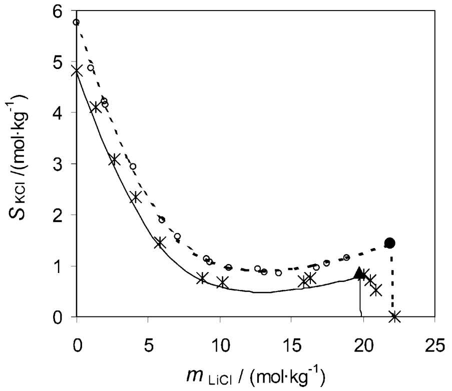

Figure 6. Experimental and literature data (symbols) and calculated isotherms (lines) at T = (298 and 323) K in the $KCl + LiCl + H_2O$ system. ★, 298 K, Akopov;[11] ○, 323 K, this work. Experimental invariant data: ▲, 298 K; ●, 323 K.

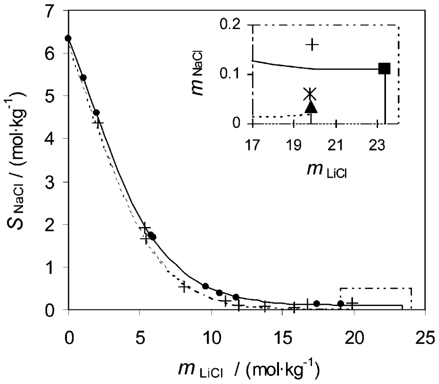

Figure 7. Experimental and literature data (symbols) and calculated (lines) isotherms at $T = (298 \text{ and } 333)$ K in the system $NaCl + LiCl + H_2O$. +, 298 K, Linke and Seidell;[7] ●, 333 K, this work. Invariant data: ★, 298 K, Sarkarov and Mironova;[5] ▲, 298 K, this work; ■, 333 K, this work.

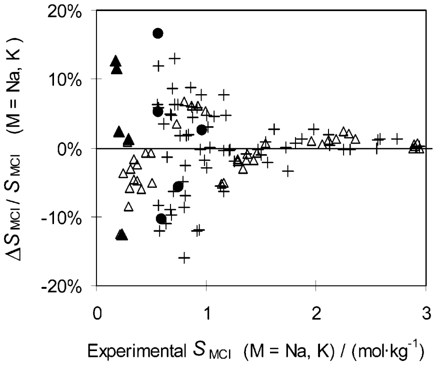

Figure 8. Relative deviations between experimental and calculated solubilities (mol·kg^{-1}) of sodium and potassium chlorides in aqueous systems with $AlCl_3{\cdot}6H_2O$. +, KCl; △, NaCl. Invariant points: ●, KCl; ▲, NaCl.

lithium chloride are largely in error. The pattern of the deviations may indicate the presence of moisture in the lithium salt that was not accounted for, thus explaining that the solubility of pure LiCl at 298 K reported by Akopov nearly coincides with the actual value at 323 K.

The predicted saturation molalities of sodium chloride in NaCl + LiCl solutions are in excellent agreement with experiment up to 12 mol·kg^{-1} LiCl. For higher concentrations of this solute, a sharp reduction of the saturation concentrations of sodium chloride is observed, and the relative deviations between the experimental and calculated values are augmented significantly. The negligible influence of temperature on the solid−liquid phase diagram of the $NaCl + LiCl + H_2O$ system is illustrated in Figure 7, where the isotherms at $T = (298 \text{ and } 333)$ K are shown. Some solubility values at 298 K found in the literature[5,7] are reasonably well reproduced by the proposed empirical equation, with a standard deviation of fit of ±0.11 mol·kg^{-1}. The contents of LiCl and NaCl reported by Sarkarov and Mironova[5] for the invariant point at 298 K nearly coincide with the experimental values obtained in this study, as shown in the enlarged section of Figure 7.

The crystallization fields of potassium and sodium chlorides in the ternary systems $KCl + AlCl_3 + H_2O$ and $NaCl + AlCl_3 + H_2O$ were also described by eqs 1 and 4, with m_{NCl}, the content of aluminum chloride, expressed as an anhydrous salt. The coefficients for the regression equations and the quality of fit are summarized in Table 14. Because of the limited number of measured solubility values in the field of hexahydrate aluminum chloride with NaCl or KCl, no attempt was made to correlate these data.

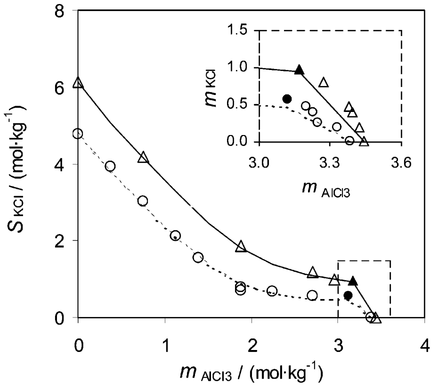

Figure 9. Experimental (symbols) and calculated (lines) isotherms at $T = (298 \text{ and } 333)$ K in the system $KCl + AlCl_3 + H_2O$: ○, 298 K; △, 333 K. Experimental invariant points: ●, 298 K; ▲, 333 K.

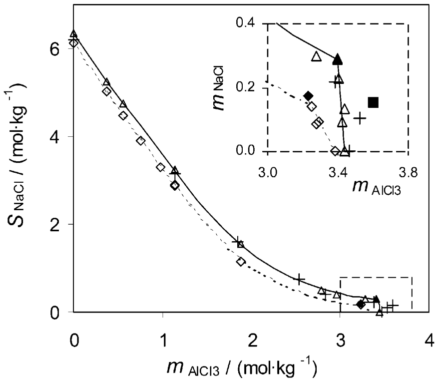

Figure 10. Literature and experimental and calculated (lines) isotherms at $T = (298 \text{ and } 333)$ K in the system $NaCl + AlCl_3 + H_2O$. +, 298 K, Sarkarov and Mironova;[5] Experimental: ◇, 298 K; △, 333 K. Invariant data: ■, 298 K, Sarkarov and Mironova;[5] ◆, 298 K, this work; 333 K ▲, this work.

The fit of the experimental solubilities of NaCl and KCl by the empirical equations is fairly good up to near the invariant-composition mixtures, although for the $AlCl_3$-rich solutions the relative deviations between the experimental solubilities and the corresponding smooth curves increase up to ±15%, as illustrated in Figure 8.

The calculated isotherms and the experimental values measured at $T = (298 \text{ and } 333)$ K in both fields of the phase diagrams of $KCl + AlCl_3 + H_2O$ and $NaCl + AlCl_3 + H_2O$ are plotted in Figures 9 and 10, respectively. To our knowledge, no solubility data for the first of these systems have been published. The only set of data[5] found in the literature for $NaCl + AlCl_3$ aqueous mixtures was included in Figure 10 for reference. The published solubilities of NaCl are systematically higher than those measured in this study, by as much as 0.3 mol·kg^{-1}, nearly superimposing the calculated isotherm at 333 K.

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