

School of Chemical Engineering NTUA Department of Process Analysis and Plant Design

Gas Purification using Pure Ionic Liquids and Ionic Liquid - Polymer mixtures as Absorbents

Diploma Thesis

submitted by

Panagiota Katherina Garbis

Supervising Professor : Nikolaos Papayannakos

Athens

August 2015

Copyright Notice

I hereby declare that I have prepared and written the enclosed diploma thesis completely on my own. I also declare that I have not used any resources or references other than stated in the thesis. An exception to this is the constant personal communications with the advisers of this work, which are therefore not declared individually. The diploma thesis was not used in the same or in a similar version to achieve an academic grading or is published elsewhere.

The utilization and exploitation of this work for teaching and research purposes, for reports and publications are granted to the University of Bayreuth, represented by the Chair of Chemical Engineering (Prof. Dr.-Ing. Andreas Jess). My contribution to publication of contents or excerpts of this work shall be indicated in an appropriate manner. I agree with the publication of my name and the subject of the thesis in the list of accomplished study-accompanying works of the Chair of Chemical Engineering. I additionally declare that I will not publish contents of this work without the approval of the Chair of Chemical Engineering.

.....

.....

Location, Date

Signature

Table of Contents

Co	opyrig	ht Noti	ce	V
Li	st of s	ymbols		IX
Al	ostrac	t		1
П	ερίληψ	þη		3
1	Intro	ductior	n and objectives of the work	7
2	Basic	theory	and background of the work	9
	2.1	lonic L	iquids	9
		2.1.1	1-Ethyl-3-methylimidazolium methanesulfonate [EMIM][MeSO ₃]	10
	2.2	Agar a	gar Kobe I	11
	2.3	Poly(v	inyl alcohol) (PVOH)	12
	2.4	Gels a	nd Ionogels	15
	2.5	The ab	sorption process	17
3	Scop	e of the	e work	21
4	Expe	rimenta	al method and data analysis	23
	4.1	lonoge	el preparation	23
	4.2	Deterr	nination of water content in poly(vinyl alcohol)	23
	4.3	Densit	y measurements with a Hubbard pycnometer	24
	4.4	Viscos	ity measurements with a Falling Ball Viscosimeter	24
	4.5	Therm	ogravimetrical analysis (TGA)	27
		4.5.1	Definition of thermogravimetrical analysis	27
		4.5.2	Sample preparation and conditioning	27
		4.5.3	Discrimination between thermal decomposition and evaporation during a TG-experiment	28
		4.5.4	The isoconversional Method	28
		4.5.5	Analysis and modeling of TG-experiments at ambient pressure and constant heating rate	32
		4.5.6	Definition of the maximum operation temperature with regard to the thermal decomposition	33
	4.6	H₂S Ab	osorption	34

		4.6.1	Experimental Set-up	34
		4.6.2	Absorption of H ₂ S in [EMIM][MeSO ₃]	37
		4.6.3	Desorption of H ₂ S from [EMIM][MeSO ₃]	38
	4.7	Gas de	hydration using ionogels	.39
		4.7.1	Experimental Set-up	39
		4.7.2	Absorption of water in the polymer mixtures	43
5	Resu	lts and	discussion	.45
	5.1	Agar a	gar Kobe I - [EMIM][MeSO ₃] mixtures	.45
	5.2	PVOH	- [EMIM][MeSO ₃] mixtures	.47
	5.3	Densit	y measurements of IL-polymer mixtures	.47
	5.4	Viscos Viscos	ity measurement of ionic liquid - polymer mixtures with the Falling Ball imeter	.49
	5.5	Charao	cterization of the IL [EMIM][MeSO $_3$] using thermogravimetric analysis data	.50
		5.5.1	Discrimination between thermal decomposition and evaporation during the TG-experiments with the ionic liquid [EMIM][MeSO ₃]	50
		5.5.2	Kinetic of thermal decomposition of [EMIM][MeSO ₃]	51
	5.6	Charao	cterization of Mowiol 56-98 and Mowiol 40-88	.57
		5.6.1	Influence of the crucible material during TG-experiments	57
		5.6.2	Dependence of the TG-signal on the initial mass of the sample	58
		5.6.3	Discrimination between thermal decomposition and evaporation during TG-experiments	58
		5.6.4	Kinetics of thermal decomposition of Mowiol 56-98 and Mowiol 40-88	59
		5.6.5	Maximum operating temperature of Mowiol 56-98 and Mowiol 40-88 with regard to thermal decomposition	61
	5.7	Therm	ogravimetrical characterization of the IL-polymer mixtures	.61
	5.8	Henry	coefficient of H ₂ S in [EMIM][MeSO ₃]	.64
	5.9	Dehyd	ration of gas with the ionic liquid [EMIM][MeSO ₃]	.66
	5.10	Dehyd	ration of gas with the PVOH - [EMIM][MeSO ₃] mixtures	.68
6	Sum	mary ar	nd Outlook	.71
7	Refe	rences		.75

List of symbols

Latin Letters

А	Material and temperature dependent constant	-
A _{abs.}	Head of the recess in the gas dehydration apparatus	m ²
В	Material and temperature dependent constant	К
С	Material and temperature dependent constant	К
$C_{\rm vap}$	Entropy term	Ра
E _a	Activation energy	J mol ⁻¹
EV	Ester value	kg KOH g⁻¹
f(X)	Reaction model	-
g(X)	Integral form of the model reaction	-
h(p)	Pressure dependency	-
G'	Storage modulus	-
G''	Loss modulus	-
Н	Henry coefficient	Ра
${\mathcal H}$	Degree of hydrolysis	mol%
HR	Heating rate	K s ⁻¹
<i>k</i> ₀	Pre-exponential factor	s ⁻¹
k(T)	Rate constant	s ⁻¹
К	Ball constant at the Falling Ball Viscosimeter	Pa m ³ kg⁻¹
m ₀	Initial mass	kg
\overline{M}_{w}	Average molar mass	kg mol⁻¹
p	Partial pressure	Ра
p^0	Reference pressure	Ра
$p_{\mathrm{i,sat}}$	Saturation vapor pressure of component i	Ра
$p_{ m vap}$	Vapor pressure	Ра

$ar{P}_{ m w}$	Average degree of polymerization	-
R	Universal gas constant	8.314 J mol ⁻¹ K ⁻¹
t	Time	S
Т	Temperature	К
T _{max}	Maximum operation temperature	К
x	Molar fraction	-
Χ	Conversion	-
z(X)	Integral form of the reaction models at the isoconver- sional method	-

Greek Letters

β	heating rate	K s⁻¹
γ	Activity coefficient	-
$\Delta H_{\rm vap}$	Evaporation enthalpy	J mol⁻¹
η	Dynamic viscosity	Pa s
$\pi(\kappa)$	Approximation for the isoconversional method	-
ρ	Density	kg m⁻³
ω	Angular frequency	rad

Abbreviations

Cupric sulfate
Differential-Thermogravimetric-Signal
Gel permeation chromatography
1-Ethyl-3-methylimidazolium methanesulfonate
Helium
1-(2-hydroxyethyl)-3-methylimidazolium tetrafluoroborate

H ₂ S	Hydrogen sulfide
IL	Ionic liquid
MFC	Mass Flow Controller
MSB	Magnetic suspension balance
NMR	Nuclear magnetic resonance spectroscopy
NTP	Normal Temperature and Pressure (T = 20 °C, p = 1,01325 bar)
N ₂	Nitrogen
ppm	Parts per million
PVOH	Poly(vinyl alcohol)
rH	Relative humidity
STP	Standard Temperature and Pressure (T = 0 °C, p = 1,01325 bar)
TEG	Triethylenglycol
TG or TGA	Thermogravimetry
wt%	Weight percent

Abstract

The interest in ionic liquids (melting point below 100°C; IL) and their potential applications are still rising in academia as well as industry due to the variety of their chemical and physical properties. In separation processes, evaporation losses and product contaminations can be avoided because of their very low vapor pressure. A number of ionic liquids have hygroscopic character, so they can absorb a certain extent of water. This property can be an advantage for gas and fluid drying.

Gas drying is an important separation process for drying of natural gas in order to avoid corrosion and hydrate formation in the pipelines. In the industry, the absorptive gas scrubbing with glycols (especially with triethylene glycol; TEG) as absorbent is well established.

The absorption of hydrogen sulfide is also of great importance in the gas industry. The toxicity and corrosive properties of H_2S dictate stringent control of its release into the environment and contact of aqueous solutions of H_2S with iron and steel as tanks, piping, valves and pumps. The most common way for the removal of acidic components from gas streams are amine solutions. In contrast to various studies on the absorption of CO_2 and SO_2 in ILs, the number of publications on absorption of water as well as hydrogen sulfide is still low. ILs could be alternative absorbents for water and hydrogen sulfide absorption too.

At the beginning of the 21. Century, ionic liquids were immobilized on porous supports in order to combine e.g. the advantages of both the homogeneous and heterogeneous catalysis. Other researchers tried to combine both the unique properties of polymers and ILs. This leads to supported membranes and the so-called "ionogels". Ionic liquids confined in gel matrices make them suitable in various applications e.g. stable electrolytes in dye-sensitized solar cells, secondary batteries, electrochromic displays, electrolytic membranes and perhaps even for gas separation processes in a kind of "fixed bed absorber".

The present work is divided in two main parts. In the first part the immobilization of the ionic liquids in a polymer matrix and the evaluation, if these hybrid materials are suitable for gas dehydration was investigated. The hygroscopic ionic liquid [EMIM][MeSO₃] was immobilized into the three polymers, the agar agar Kobe I and two types of poly(vinyl alcohol) (PVOH) Mowiol 56-98 and Mowiol 40-88. The occurred fouling due to the high amount of water in the agar agar-[EMIM][MeSO₃] ionogels was the reason why the PVOH-[EMIM][MeSO₃] ionogels were chosen for the gas dehydration. First the main components of the ionic liquid – polymer mixtures were characterized. The thermal decomposition of the [EMIM][MeSO₃] was calculated with a "model free" method, the isoconversional method ($E_a = 137$ kJ mol⁻¹, $k_0 = 6.2 \cdot 10^8$ s⁻¹) and compared with literature data. The calculation of the kinetics of thermal decomposition using the isoconversional method took considerable time without having any advantage com-

pared to the TGA-method established at the Chair of Chemical Engineering of University of Bayreuth. At next the thermal decomposition of the two types of PVOH (Mowiol 56-98, Mowiol 40-88) was also determined with the TGA method ($E_a = 175 \text{ kJ mol}^{-1}$, $k_0 = 7.89 \times 10^{13} \text{ s}^{-1}$). Furthermore the density and viscosity of the prepared IL - polymer mixtures were measured. Based on the results the IL - polymer mixtures with about 10 wt% PVOH in [EMIM][MeSO₃] were chosen for the gas dehydration measurements. Therefor a dehydration plant was build up. The experiment was accomplished at an absorbent temperature of 42 °C and three different dew points of the feed gases. Comparison of the activity coefficients of water in the ionogels compared with the activity coefficients of water in the pure ionic liquid show no measurable deviation from each other. This means that the polymer matrix doesn't influence the absorption capacity of the ionic liquid in greater extend.

In the second part of this study, the absorption of the hydrogen sulfide was accomplished using the [EMIM][MeSO₃] as an absorbent. The measurements showed that the ionic liquid [EM-IM][MeSO₃] is suitable for the purification of gas from its hydrogen sulfide component. For the absorption temperature of 22 °C, the Henry coefficient of H₂S in the [EMIM][MeSO₃] is 3 924 mbar and by a factor of about 1.5 lower compared to the N-methylpyrrolidone at 20°C. The Henry coefficient of the H₂S in [EMIM][MeSO₃] for a temperature of 32 °C is 5 041 mbar and by a factor of 5,7 lower compared to the ionic liquid [hemim][BF₄] at a temperature of 30 °C.

In conclusion, the present work shows that the ionic liquid $[EMIM][MeSO_3]$ can be immobilized into the polymer poly(vinyl alcohol) without losing its absorption capacity. On the basis of the results, the main idea to get a kind of "fixed bed absorber" seems to be possible since the IL - polymer mixtures keep the absorption capacity of the ionic liquid. Further studies concerning the ternary mixtures H₂O - IL - polymer should be conducted in order to get more information about the mechanism of gelation, rheological behavior, miscibility gaps and informations about the mass transfer in such a gel layer.

The investigation on separating the hydrogen sulfide (H₂S) with the ionic liquid [EM-IM][MeSO₃] from a gas stream showed that the [EMIM][MeSO₃] has a good absorption capacity. It is already proven that the [EMIM][MeSO₃] is an alternative drying agent to the absorbent TEG commonly used for industrial gas drying. In the ideal case, both gases would be absorbed simultaneously. Therefor it should be furthermore investigated if the [EMIM][MeSO₃] can also separate H₂S from natural gas in presence.

Both the experimental part and the written composition of this work were conducted during a stay at the Chair of Chemical Engineering at the University of Bayreuth, which was funded by the Erasmus Exchange Programme.

Περίληψη

Το ενδιαφέρον για τα ιοντικά υγρά (σημείο τήξης < 100 °C) και των πιθανών εφαρμογών τους, αυξάνονται συνεχώς τόσο στον ακαδημαϊκό όσο και στον βιομηχανικό τομέα λογω των ποικίλων χημικών και φυσικών τους ιδιοτήτων. Σε διεργασίες διαχωρισμού, οι απώλειες λόγω εξάτμισης και οι μόλυνση των προϊόντων μπορούν να αποφευχθουν χάρη στην πολύ χαμηλή πίεση ατμών τους. Κάποια ιοντικά υγρά έχουν υγροσκοπικό χαρακτήρα, απορροφόντας μια σημαντική ποσότητα νερού. Η ιδιότητα αυτή αποτελεί σημαντικό πλεονέκτημα για την χρήση τους στην ξήρανση υγρών και αερίων.

Η ξήρανση του φυσικού αερίου αποτελεί σημαντική διαδικασία για την αποφυγή διαβρώσεων και σχηματισμού υδρατμών στις σωληνώσεις. Η πλεον εδραιωμένη ξήρανση του φυσικού αερίου στον βιομηχανικό τομέα πραγματοποιείται με την χρήση γλυκολών και ειδικότερα της τριαιθυλενογλυκόλης (TEG).

Μεγάλη σημασία στην βιομηχανία του φυσικού αερίου έχει επίσης η απομάκρυνση του υδρόθειου. Η τοξικότητα και οι διαβρωτικές ιδιότητες του υδρόθειου υπαγορεύουν αυστηρό έλεγχο περιορισμού της απελευθέρωσης του στο περιβάλλον και επαφής του με σίδηρο και χάλυβα όπως για παραδειγμα σε δεξαμενές, σωληνώσεις, βαλβίδες και αντλίες. Ο πιο συνηθισμένος τρόπος απομάκρυνσης των όξινων συστατικών απο ρεύματα αερίου είναι τα διαλύματα αμινών.

Αντίθετα με τις διάφορες μελέτες απορρόφησης CO₂ και SO₂, ο αριθμός των δημοσιεύσεων σχετικά με την απορρόφηση νερού (υδρατμών) καθώς και υδρόθειου εξακολουθεί να είναι χαμηλός. Τα ιοντικά υγρά θα μπορούσαν να αποτελέσουν ένα εναλλακτικό μέσο απορρόφησης νερού και υδρόθειου.

Στις αρχές του 21^{ου} αιώνα, ξεκίνησε η προσπάθεια σταθεροποίησης τους σε πορώδη υλικά ώστε να συνδιαστούν τα πλεονεκτήματα τους τόσο στην ομογενή όσο και στην ετερογενή κατάλυση. Άλλοι ερευνητές ξεκίνησαν προσπάθειες συνδυασμού τους με πολυμερή ελπίζοντας στον συνδυασμό των ιδιοτήτων τους. Ο συνδυασμός αυτός οδήγησε στα λεγόμενα "ionogels" και καθίστανται κατάλληλα σε διάφορες εφαρμογές (ηλεκτρολυτικές μεμβράνες, ηλεκτροχρωμικές οθόνες κτλ.) και ίσως ακόμη σε διεργασίες διαχωρισμού αερίων σε σταθερή κλίνη απορρόφησης.

Η παρούσα εργασία χωρίζεται σε δύο κύρια μέρη. Στο πρώτο μέρος, γίνεται συνδυασμός των ιοντικών υγρών με πολυμερή και αξιολόγηση τους στην ξήρανση αερίων. Το υγροσκοπικό ιοντικό υγρό [EMIM][MeSO₃] συνδυάστηκε με τρια πολυμερή υλικά, agar agar και δύο τύπους βινυλικής αλκοόλης (PVOH) το Mowiol 56-98 και Mowiol 40-88. Η μεγάλη ποσότητα νερού στα agar agar - [EMIM][MeSO₃] ionogels ήταν ο λόγος για την επιλογή των PVOH - [EMIM][MeSO₃] ionogels για τα πειράματα ξήρανσης αερίου. Αρχικά έγινε χαρακτηρισμός

των συστατικών των μιγμάτων ιοντικών υγρών - πολυμερών. Η θερμική αποσύνθεση του [EMIM][MeSO₃] υπολογίστηκε με μια μέθοδο ¨ελευθερου μοντέλου¨, την isoconversional method ($E_a = 137 \text{ KJ mol}^{-1}$, $k_0 = 6,2 \ 10^8 \text{ s}^{-1}$) και συγκρίθηκε με δεδομένα της βιβλιογραφίας. Ο υπολογισμός της κινητικής της αποσύνθεσης χρησιμοποιώντας αυτή τη μέθοδο ήταν χρονοβόρος χωρίς κάποιο πλεονέκτημα σε σχέση με την θερμοσταθμική μέθοδο (TGAmethod) που αναπτύχτηκε στο Chair of Chemical Engineering, University of Bayreuth. Στην συνέχεια η θερμική αποσύνθεση των δύο τύπων βινυλικής αλκοόλης Mowiol 40-88) προσδιορίστηκε με την θερμοσταθμική (Mowiol 56-98, μέθοδο (E_a = 175 KJ mol⁻¹, k₀ = 7,89 10¹³ s⁻¹). Επιπλέον πραγματοποιήθηκαν μετρήσεις της πυκνότητας και του δυναμικού ιξώδους των μιγμάτων ιοντικού υγρού - πολυμερούς. Με βάση τα αποτελέσματα των παραπάνω μετρήσεων τα μείγματα με περίπου 10 % κ.β. ΡVOH στο ιοντικό υγρό [EMIM][MeSO₃] επιλέχθηκαν για τις μετρήσεις ξήρανσης αερίου. Για τον σκοπό αυτό κατασκευάστηκε εγκατάσταση για μετρήσεις απορρόφησης υδρατμών από αέρια ρεύματα. Τα πειράματα πραγματοποιήθηκαν σε θερμοκρασία απορροφητικού υλικού 42 °C και τρια διαφορετικά σημεία δρόσου των αερίων τροφοδοσίας. Ο συντελεστές ενεργότητας των μετρήσεων απορρόφησης υδρατμών στα ionogels συγκρίθηκαν με τους συντελεστες ενεργότητας απορρόφησης υδρατμών στο καθαρό ιοντικό υγρό [EMIM][MeSO₃]. Οι αποκλίσεις ήταν μηδαμινές και μη μετρήσιμες. Συμπερασματικά η δομή του πολυμερούς δεν επηρεάζει σε μεγάλο βαθμό την απορροφητική ικανότητα του ιοντικού υγρού.

Στο δεύτερο μέρος της εργασίας επιτεύχθηκε απορρόφηση υδροθείου χρησιμοποιώντας ως απορρόφητικό μέσο το ιοντικό υγρό [EMIM][MeSO₃]. Οι μετρήσεις έδειξαν πως το ιοντικό υγρό είναι κατάλληλο για την απομάκρυνση του υδροθείου απο αέρια ρεύματα. Στην απορρόφηση σε θερμοκρασία 22 °C ο συντελεστής Henry του H₂S στο [EMIM][MeSO₃] είναι 3924 mbar και κατά έναν παράγοντα περίπου 1,5 χαμηλότερος από εκείνον της N-μεθυλοπυρρολιδόνης στους 20 °C. Ο συντελεστής Henry του H₂S στο [EMIM][MeSO₃] σε θερμοκρασία 32 °C είναι 5041 mbar και κατά έναν παράγοντα περίπου 5,7 χαμηλότερος από εκείνον του ιοντικού υγρού [hemim][BF₄] στους 30 °C.

Συμπερασματικά η παρούσα εργασία παρουσιάζει τον συνδυασμό του ιοντικού υγρού [EMIM][MeSO₃] με πολυμερή, διατηρώντας τις ιδιότητες και των δύο συστατικών. Με βάση τα αποτελέσματα, η βασική ιδέα δημιουργίας ενός είδους σταθερής κλίνης απορρόφησης φαίνεται να είναι πραγματοποιήσιμη αφού διατηρείται η ιδιότητα απορρόφησης του ιοντικού υγρού. Θα πρέπει να διεξαχθούν περαιτέρω μελέτες λαμβάνοντας υπόψη σε σημαντικό βαθμό την ποσότητα νερού στα μίγματα. Τριμερή μίγματα νερού - ιονικού υγρού πολυμερούς θα εξεταστούν για την λήψη πληροφοριών σχετικά με τον μηχανισμό πήξης, την ρεολογική συμπεριφορά και ανάμειξη των συστατικών.

Η έρευνα του διαχωρισμού του υδρόθειου απο ένα αέριο ρεύμα έχοντας ως απορροφητικό μέσο το [EMIM][MeSO3] έδειξε ότι έχει μια πολύ καλή ικανότητα απορρόφησης. Θα πρέπει

να γίνουν περεταίρω μελέτες για τον διαχωρισμό του υδρόθειου από ρεύμα φυσικού αερίου. Έχει ήδη αποδειχθεί ότι το [EMIM][MeSO₃] είναι μια εναλλακτική λύση για την ξήρανση του φυσικού αερίου στην βιομηχανία. Στην ιδανική περίπτωση τόσο το νερό όσο και το υδρόθειο θα απορροφούνται ταυτόχρονα.

Το πειραματικό μέρος και η γραπτή σύνθεση της εργασίας πραγματοποιήθηκαν κατά την διάρκεια παραμονής στο Chair of Chemical Engineering, University of Bayreuth στα πλαίσια του προγράμματος ανταλλαγής φοιτητών Erasmus.

1 Introduction and objectives of the work

Gas dehydration/purification is a very important separation process in industry like e.g. the dehydration of natural gas to avoid corrosion and formation of hydrates in pipelines [1–3]. Therefor the most commonly used industrial process is the absorption of the water vapor with glycols. In the early 1930s, diethylene glycol (DEG) was the first absorbent to dry natural gas in dehydration plants. Triethylene glycol (TEG) was also proved to be very effective [1,4]. However, TEG has two major disadvantages:

- TEG has a relatively high vapor pressure [5] and
- TEG is not stable against oxidative attack. Hence, the regeneration of water loaded TEG is not straightforward. A distilling unit with temperatures up to 573 K is commonly used to avoid high evaporation losses and contact with air has to be avoided [6,7].

Now the question arises: What is an ideal solvent for gas dehydration? An ideal solvent for dehydration of a gas by absorption/scrubbing of water vapor should have the following properties:

- The partial pressure of the solvent should be as low as possible to avoid evaporation losses.
- The affinity of the solvent to water vapor should be high, i.e., the water vapor pressure of the solvent/water mixture should be as low as possible.
- The solvent should be robust with regard to thermal decomposition and to a chemical attack by oxygen.
- The absorption agent should be non-toxic.

lonic Liquids (ILs) are often defined as low melting salts with a melting point below 373.15 K. Since their discovery, the number of potential applications of neat ILs is still rising in academia as well as in industry. This is due to the wide variety of their chemical and physical properties which can be modified by combinations of different anions and cations [8–12]. These often so-called "designer solvents" [13,14] represent a new and promising solvent class, e.g. for homogeneous (two-phase) catalysis [10,15,16] and for separation processes like extractions [17,18] and other applications which have been reviewed various publications [9,19].

One main reason that ILs have gained interest in both academia and industry is that they have an extremely low vapor pressure. The hydrophilic ionic liquid 1-ethyl-3-methylimidazolium methanesulfonate ([EMIM][MeSO3]) shows an extremely low vapor pressure at ambient temperature compared to common solvents like TEG and a relatively high thermal and oxidative stability at elevated temperatures up to 423 K. This makes it very attractive for separation processes like the natural gas dehydration, since losses by evaporation and thus impurities in product streams can be avoided [20].

At the beginning of the 21. Century, ionic liquids were immobilized on porous supports in order to combine e.g. the advantages of both the homogeneous and heterogeneous catalysis [21–24]. Other researchers tried to combine both the unique properties of polymers and ILs. This leads to supported membranes and the so-called "ionogels"[21]. Ionic liquids confined in gel matrices makes them suitable in various applications e.g. stable electrolytes in dyesensitized solar cells, secondary batteries, electrochromic displays, electrolytic membranes [25] and perhaps even for gas separation processes.

This leads to the two main objectives of this work: The first objective is to investigate the absorption of H_2S in the neat ionic liquid [EMIM][MeSO₃], which is a common impurity besides water vapor in natural gas. This may expand the possible applications of this IL to other gas purification processes. Therefore, the Henry coefficient of hydrogen sulfide is measured at different temperatures and is compared to literature data.

The second objective concerns the immobilization of the ionic liquids in a polymer matrix and the evaluation, if these hybrid materials are suitable for gas dehydration. In this case, the main idea is to get a kind of "fixed bed absorber". For these purpose two different commercially available polymers, the agar agar Kobe I and the poly(vinyl alcohols) Mowiol 56-98 and Mowiol 40-88, were used. The obtained hybrid materials were characterized in terms of thermal stability, viscosity, density and dehydration capability in a dehydration plant.

The present work was co-operated with the University of Bayreuth at the Chair of Chemical Engineering of Prof. Dr.-Ing. Andreas Jess. The experimental procedure were performed at the Chair of Chemical Engineering at the University of Bayreuth. In the following, Chapter 2 gives an overview about the theoretical background. The scope of this work and the conducted measurements are described in Chapter 3. The description of the experimental set-ups and the used measurement methods follows in Chapter 4. The results of this work are presented and discussed in Chapter 5. Finally, a summary and an outlook are given in Chapter 6.

2 Basic theory and background of the work

This chapter gives an overview of the theoretical background that has to be known for understanding the following work. At first, the physical properties of the ionic liquid [EMIM][MeSO₃] and the polymers agar agar Kobe I and poly(vinyl alcohols), that are used in this work for the production of the ionogels, are described. Afterwards a kinetic computation on thermal analysis data known as isoconversional method is explained. The computation of the kinetic parameters with regard to thermal decomposition of the ionic liquid [EMIM][MeSO₃], the polymer poly(vinyl alcohol) and the produced ionogels are described. Furthermore the absorption process is described and the calculations of the parameters that quantify the absorption capacity are presented.

2.1 Ionic Liquids

In the last 10 years the scientific interest in ionic liquids (ILs) increased rapidly. Ionic liquids are low melting salts with melting point under 100 °C [8]. They consist exclusively of ions or almost exclusively of ions such as protic ionic liquids (ethylammonium nitrate) and therefore exhibit ionic conductivity [9]. Ionic liquids have a huge variety of chemical and thermophysical properties [26,27].

One of the features of ionic liquids is the broad variation of their solubility and miscibility properties. They can, for example dissolve both ionic and covalent compounds. This feature makes them attractive not only as solvents and electrolytes in electrochemical reactions and chemical processes, but also for the separation and extraction of materials from solutions and mixtures [9,28]. They are also good solvents for a wide range of both organic and inorganic materials and can be brought into the same phase with unusual combinations of reagents. However, a number of organic solvents are immiscible with them, so they provide a non-aqueous, polar alternative for two-phase systems [10].

Another reason why ionic liquids gained scientific interest is their extremely low vapor pressure (e.g., ca. 10^{-10} Pa at 298 K for [C₄mim][PF₆] [29] compared with $3 \cdot 10^3$ Pa at 298 K for H₂O [30]) and low flammability. That makes them attractive for separation processes, avoiding losses by evaporation in product steams [31,32]. These characteristics make ionic liquids promising candidates in the field called "Green Chemistry" as a substitute for currently used toxic, flammable and volatile solvents [9,14,28,33].

This work is based on the ionic liquid [EMIM][MeSO₃]. Therefore physical properties of this ionic liquid will be described hereinafter in detail.

2.1.1 1-Ethyl-3-methylimidazolium methanesulfonate [EMIM][MeSO₃]

The ionic liquid 1-ethyl-3-methylimidazolium methanesulfonate, [EMIM][MeSO₃] was purchased from Sigma-Aldrich (BASF quality, purity of \geq 95 wt%). The molecular formula is C₆H₁₁N₂ · CH₃O₃S. The structural formula of [EMIM][MeSO₃] is shown in Figure 1.



Figure 1: Structural formula of [EMIM][MeSO₃].

In the following the physical properties with relevance for this work are presented in Table 1.

Table 1: Properties of [EMIM][MeSO₃] with relevance for this work.

Molar mass in g mol ⁻¹ [34]	206.26
Melting point in °C [35]	31
Density in kg m ⁻³ [32]	1240 (T = 298.15 K)

The activity coefficient of the binary mixture of [EMIM][MeSO₃] and water has been measured in the past at the Chair of Chemical Engineering of the University in Bayreuth. For temperatures between 30-50°C the activity coefficient is given by Eq. (2.1).

$$\gamma_{\rm H_2O}(x_{\rm H_2O},T) = 0.925 \cdot x_{\rm H_2O}^{2.7} + 0.075 \qquad 30^{\circ}{\rm C} < \theta < 50^{\circ}{\rm C}$$
(2.1)

The vapor pressure of [EMIM][MeSO₃] can be calculated through the Arrhenius equation (Eq. (2.2)) for $C_{\text{vap}} = 7.5 \cdot 10^{12} \text{ Pa}$, $\Delta_{\text{vap}}H = 141.0 \text{ kJ mol}^{-1}$ [36].

$$p_{\rm vap} = C_{\rm vap} \cdot e^{-\frac{\Delta_{\rm vap}H}{R \cdot T}}$$
(2.2)

where p_{vap} is given in Pa and T in K

The activity coefficient of the mixture [EMIM][MeSO₃] and H₂S will be measured and presented in this work. The ionic liquid [EMIM][MeSO₃] was used not only for the absorption of hydrogen sulfide and water but also in a combination with the polymers presented in the following section for the preparation of the ionogels.

2.2 Agar agar Kobe I

Agar agar Kobe I or agar is a hydrophilic colloid extracted from seaweeds of the Rhodophyceae class [37,38]. The raw material of agar can be of different seaweeds like different species of gelidium but also species of gracilaria, pterocladia capillace and gelidiella, depending on the country where they are produced [39].

Early studies showed that agar is a polysaccharide that is composed entirely of galactose residues which are arranged in chains with galactose repeating units [40]. Nowadays it is established that agar consists of two fractions, agarose and agaropectin [39]. Agar is composed of alternating D-galactose and 3,6-anhydro-L-galactose repeating units. Agarose, the gelling component is a sulfate free polysaccharide and its basic sugar units are D-galactose, L-galactose, 3,6-anydro-L-galactose and D-xylose. Agaropectin is a non-gelling ionic polysaccharide and includes a small amount of sulfate ($\approx 2\%$). Its basic sugar units are D-galactose, L-galactose, 3,6-anydro-L-galactose, D-xylose, galactose sulfate and pyruvic acid [41,42].

Agar molecular formula of is $[-C_{12}H_{18}O_{9}-]_n$. Its molecular structure is shown in Figure 2.



Figure 2: Molecular structure of agar agar.

In this work agar agar Kobe I was purchased from Carl Roth. The properties of this gelator are shown in Table 2. The gel strength is a measure of the ability of a colloidal dispersion to develop and retain a gel form. There are different techniques for measuring the gel strength like the Bloom test, the Nikan-Sui method (extended Kobe method) and various other rheometric techniques. The Bloom test for instance gives the gel strength in terms of the force required to depress a plunger of given diameter, set on a gel surface, a distance of 4 mm. To the contrary, the Nikan-Sui method measures the force required to the point of rupture of the gel in a certain time [39,43].

Density	0.55
Gel strength (1.5% gel)	\geq 1000 g/cm ²
Gelling Temperature	35 -42 °C
Moisture	≤ 15 %
pH-value	5.0 -8.0
Ash	≤ 1.5 %

 Table 2:
 Properties of agar agar Kobe I [44].

An important property of the gelation with agar is that it has an excellent thermal reversibility allowing it to be repeatedly gelled and melted without losing any of the original properties [45]. However the large number of hydroxyl groups makes agarose insoluble in cold water and many common organic solvents. Agar gels find numerous applications in various fields such as food gelation (jams, candies, ice creams etc.) in the food industry, dental molds and pharmaceutical formulations, electrophoresis, tissue engineering or a matrix of soft-matter organic devices. [25,41].

Agar was used for the agar-[EMIM][MeSO₃] ionogels, which will be described in the chapter 4. The ionogels will also be produced from the mixture of poly(vinyl alcohol) and [EM-IM][MeSO₃]. Important properties of the poly(vinyl alcohol) are presented in the following section.

2.3 Poly(vinyl alcohol) (PVOH)

Poly(vinyl alcohols) are watersoluble polymers of vinyl alcohol [46]. The monomer, however, has been neither isolated nor obtained in a high concentration. Thus PVOH is a special synthetic polymer, that cannot be prepared by polymerization of the corresponding monomer [47].

In this work was used PVOH from Kuraray. Its molecular formula is $[-CH_2CHOH_]_n$. Its structural formula is shown in Figure 3.



Figure 3: Structural formula of poly(vinyl alcohol).

The ester of vinyl alcohol is vinyl acetate, which is the raw material for its production. The poly(vinyl acetate) dissolved in methanol is converted to poly(vinyl alcohol) by hydrolysis (alcoholysis). The catalyst is sodium hydroxide. By varying the catalyst concentration, reaction temperature and reaction time, it is possible to adjust the residual acetyl group content. In the chemistry and use of poly(vinyl alcohol), a distinction is therefore drawn between »fully and partially hydrolyzed« grades [48].

The degree of crystallization in a poly(vinyl alcohol) has a major influence on the solubility and swellability of the polymer [47]. The partially hydrolyzed grades may be considered as mixed polymers of vinyl alcohol and vinyl acetate. The degree of hydrolysis \mathcal{H} indicates the percentage of the basic polyvinyl acetate is hydrolyzed to polyvinyl alcohol. Complete hydrolysis means that the PVOH has no acetyl groups. In most of the partially hydrolyzed polyvinyl alcohol grades the acetyl content is generally about 11 wt%, corresponding to approx. 88 mol% hydrolysis in the basic poly(vinyl acetate) and 140 mg KOH/g. The degree is calculated by using Eq. (2.3)

$$\mathcal{H} = \frac{100 - 0.1535 \, EV}{100 - 0.0749 \, EV} 100 \quad \text{mol}\% \tag{2.3}$$

where EV is the "ester value" which shows the number of mg KOH needed to neutralize the acid released from the ester by saponification of 1 g of substance [48].

The fully hydrolyzed poly(vinyl alcohols) are in the range from about 97 to 100 mol% hydrolysis and produces very clear differences in the property profiles. The crystallization tendency increases very sharply in this range having as a result a reduction in the cold-water solubility of the poly(vinyl alcohol) [48].

PVOH has been used successfully in a wide range of applications for many years, thanks to its physical and chemical properties and the ability of its large number of hydroxyl groups to react with other substances [46]. The special properties of Mowiol are:

- Excellent film formation and film stability
- Stable to organic solvents
- Temperature resistant
- Highly elastic
- Soluble in water
- Specific colloid chemistry properties

One of the various names of poly(vinyl alcohol) is Mowiol. Many different types of Mowiol exist depending on the dynamic viscosity and the degree of hydrolysis (saponification) of the PVOH. To make them distinctive many manufacturer use a marking consisting of two num-

bers. The first number of this marking shows the dynamic viscosity in mPa s and the second one shows the degree of hydrolysis (saponification) in mol %. In this work Mowiol 56-98 and Mowiol 40-88 are used. The Mowiol 40-88 has a partially hydrolyzed grade while the Mowiol 56-98 has a fully hydrolyzed grade. Table 3 shows the kinematic viscosity and the degree of hydrolysis of the two Mowiol types [46,48].

	Dynamic viscosity	Degree of hydrolysis
	in mPa s	in mol%
Mowiol 40-88	40 ± 2.0	87.7 ± 1.0
Mowiol 56-98	56 ± 4.0	98.4 ± 0.4

Table 3: Dynamic viscosity and degree of hydrolysis of the used Mowiol types.

*dynamic viscosity of a 4% aqueous solution at 20°C

Table 4 shows the molar mass and the degree of polymerization of Mowiol grades. The molar mass and degree of polymerization are given by the average molar mass \overline{M}_{w} and degree of polymerization \overline{P}_{w} in relation to their molecular size. The molar mass measurements on the PVOHs themselves show often false results. Therefore it is often calculated from the molar mass values of the poly(vinyl acetates) used to manufacture the poly(vinyl alcohols). For the following grades, the mean molar mass was determined by gel permeation chromatography (GPC) combined with static light scattering on re-acetylized specimens. The accuracy of the \overline{M}_{w} was estimated at ± 15%. The degree of polymerization was calculated using Eq. (2.4) [48]:

$$\bar{P}_{\rm w} = \frac{\bar{M}_{\rm w}}{(86 - 0.42 \cdot \text{degree of hydrolysis})}$$
(2.4)

	Linear formula	Average molar mass $(\overline{M}_{ m w})$ in kg mol $^{ extsf{-1}}$	Average degree of polymerization ($ar{P}_{ m w}$)
Mowiol 40-88	[-CH ₂ CHOH-] _n	205	4200
Mowiol 56-98	[-CH ₂ CHOH-] _n	195	4300

Table 4: Mean molar mass and degree of polymerization of the used Mowiol types.

The dynamic viscosity depends on the concentration of the Mowiol in the solution. At Mowiol solutions, the dynamic viscosity rises rapidly. As a consequence, it's difficult to reach very high concentrations of Mowiol in the solutions. The dynamic viscosity also increases when the solution stands for some time at room temperature or below [48].

During heating, polymers degrade forming low molecular products. For typical vinyl polymers degradation involves breaking of C-C bonds whose bond energy is around 350 kJ mol⁻¹. Although this energy demand is large, vinyl alcohols readily degrade above 200-300 °C [49].

The described polymers were used in this work to gelate the ionic liquid [EMIM][MeSO₃]. The definition of a gel in general and especially an ionogel is given in the following section. Furthermore physical as well as chemical properties of gels are discussed.

2.4 Gels and lonogels

Different opinions exist about the definition of a gel. It is difficult to define them as a material class. The IUPAC definition of a gel is: "A gel is a nonfluid colloidal network or polymer network that is expanded throughout its whole volume by a fluid" [50,51]. Generally, a gel is a colloid and can be defined as an intermediate state that has a liquid as also solid rheological behavior. It consist of a solid network which is interspersed by a liquid [52–55].

A gel can be categorized in physical and chemical gels. Chemical gels have the polymer molecules linked through covalent bonds while physical gels have formed all their structure only by polymer molecules which are aggregate through hydrogen bonds. Physical gels have the property to hold a great amount of liquids in the interior network (most of its applications water). For example the gelation of agar produces physical gels produced by hydrogen bonds [56,57].

The polymerization of a monomer solution displays the transition from the sol state to the gel state. In the sol state, monomers start to agglomerate, forming small clusters. At a specific point, called the gel point, these clusters consolidate to form a giant network [58]. The IUPAC definition of the gel point is: "Gel point is the point of incipient network formation in a process forming a chemical or physical polymer network." The gel point is often detected using rheological methods. However different methods give different gel points. The reason therefor is, that the viscosity is tending to infinity at the gel point and a unique value cannot be measured directly [51].

The rheological behavior can be determined with oscillatory shear measurements. By subjecting a specimen to an oscillatory stress (σ) and determining the response, both the elastic and viscous or damping characteristics can be obtained. A cone is forced into oscillatory shear (angular frequency ω) or rotation. When oscillatory shear measurements are performed in the linear viscoelastic regime, the storage modulus G' (elastic response) and loss modulus G'' (viscous behavior) are independent of the strain amplitude. The dynamic viscosity can be determined as $\eta = G''/\omega$. For incipient gels at the gel point, G' and G" are expected to obey power laws in frequency:

$$G' \sim G'' \sim \omega^n \tag{2.5}$$

where n is the relaxation exponent [59,60].

As already mentioned in Section 2.2, ionic liquids have attracted the attention in the chemistry field. However, it could be desirable to immobilize the ILs in a solid device while keeping their task specific properties. This may be achieved by hybridizing ILs with low molecular weight organic gelators or polymers, which are called ionogels. Ionogels are expected to possess both the chemical versatility of the ionic liquid and the morphological versatility of a polymer [21,25,41,61].

lonogels can be characterized as host – guest complexes. The larger molecule can be considered as the host component (polymer) in which the guest molecule (smaller molecule) is encompassed [62,63]. The ionic liquid represents the guest molecule. Figure 4 shows the gelation of an IL/polymer. At high temperatures the mixture is liquid. When the mixture undergoes the gelation temperature, an ionogel is formed.



Figure 4: Schematic illustration of the gelation of an IL/polymer by changing the temperature. The arrow is bidirectional only for thermoreversible gelation.

lonogels have already been used in many applications. They take part in catalysis, biocatalysis and as electrolytes. Furthermore, they offer new ways to design conducting materials for electrochemical devices, such as batteries, fuel cells, electrochromic windows or photovoltaic cells [14]. Ionogels show multiple advantages such as tunable solubility, adjustable chain flexibility, relatively high ionic conductivity or ionic responsiveness [22].

In this work the use of ionogels of the IL [EMIM][MeSO₃] based on agar agar and PVOH are characterized. The ionogels of PVOH are also going to be used for the absorption of water from a gas stream. The absorption process will be described in detail in the following section.

2.5 The absorption process

The process where a gas component is selectively dissolved by contact with a liquid in which the component is soluble is called absorption [64]. The absorption capacity of an absorber depends on the equilibrium concentrations between gaseous phase and the liquid [65,66].

Absorption may be either chemical or physical or a combination of both. The difference is that the physical absorption involves the solubility and the vapor pressure relationships while chemical absorption involves a reaction of the primarily physically absorbed solute with the absorbing medium. Thus, chemical absorption is always combined with physical absorption such as the absorption of hydrogen sulfide (H_2S) in an amine solution [64].

The absorption of hydrogen sulfide is of great importance in the gas industry. The removal and disposal of hydrogen sulfide is the most common problem. The toxicity and corrosive properties of H₂S dictate stringent control of its release into the environment and contact of aqueous solutions of H₂S with iron and steel as tanks, piping, valves and pumps [67,68].

The most common way for the removal of acidic components from gas streams are amine solutions. In 1930 Bottoms described that the ethanolamines (diethanolamine and triethanolamine) were the most satisfactory compounds for the removal of acid components because of their high absorption capacity and their availability at a reasonable price [69,70]. Aqueous monoethanolamine and diethanolamine solutions were almost exclusively used for many years for the removal of H_2S and CO_2 from natural and certain synthesis gases[1,71–73]. Although they are rapidly being replaced by other more efficient systems, particularly for treatment of high pressure natural gases, monoethanolamine is still the preferred solvent for gas streams containing relatively low concentrations of H₂S and CO₂ and essentially no minor contaminants such as COS and CS₂. Especially when gases are treated at low pressures and maximum removal of H₂S and CO₂ are required. Its advantages are the low molecular weight of monoethanolamine, resulting in high solution capacity at moderate concentrations (on a weight basis), its high alkalinity and the relative easy regeneration possibility [1]. Using this method, purities of 1 to 4 ppm of hydrogen sulfide could be achieved [4]. However in the waste gas, the mass concentration of 3 mg/m³ (\approx 2 ppm) and the mass flow of 15 g/h of hydrogen sulfide should not be exceed [74].

Another important separation process is the gas dehydration for drying of natural gas (dewpoint (TP) of dry natural gas: -5 ° C to -15 ° C [1,36]), in order to suppress corrosion and hydrate formation in pipelines [1–3]. The dew point is the temperature, at which the water vapor containing in the gas, starts to condense (100% relative humidity) [75,76].

In the industry, several methods for gas drying are employed. The first method was based on cooling the moist gas to the required dew point, achieving a separation of the condensate [1,4]. The achievable dew point is limited to about 15 °C, when no special cooling processes are used [77]. The most common gas drying process is the absorption of water through liquid solvents (absorptive gas scrubbing) [1,4]. In the industry glycols are used as absorbents for the absorptive gas dehydration of natural gas. In the early 1930s, diethylene glycol (DEG) was the first absorbent to dry natural gas in dehydration plants. Triethylene glycol (TEG) was also proved to be very effective. Over the next 60 years the number of glycol-type natural gas dehydration plants grew to more than 20 000 in the U.S. and Canada [1].

In order to describe an absorption process, two laws have to be known depending on the molar fraction of the gas component.

For ideal mixtures, Raoult's law is valid for all solvents that approach purity and the partial pressure of component i is given by Eq. (2.6)

$$p_i = x_i p_{i,sat}(T) \quad \text{for } x_i \to 1$$
 (2.6)

where as p_i is the partial pressure in bar, x_i is the molar fraction of the component in the mixture and $p_{i,sat}$ is the saturation vapor pressure in bar at a given temperature.

Sufficiently diluted solutions whose molar fraction of component i approach zero, obey to Henry's law. According to Henry's law, the amount of a given gas that dissolves in a given type and volume of liquid is directly proportional to the partial pressure of that gas in equilibrium with that liquid, at a constant temperature.

$$p_{\rm i} = H_{\rm i} x_{\rm i} \quad \text{for } x_{\rm i} \to 0$$
 (2.7)

where H_i is the Henry coefficient in bar. In most cases, by increasing the temperature the gas solubility decreases and as a consequence, the Henry coefficient increases. An exception is hydrogen, where the solubility in hydrocarbons increases with the temperature [64].

For non-ideal mixtures Eq. (2.6) can be modified by the activity coefficient $\gamma_i(x_i, T)$. The activity coefficient is a factor used to account for deviations from ideal behavior in a mixture of chemical substances [78].

$$p_{\rm i} = \gamma_{\rm i}(x_{\rm i}, T) x_{\rm i} p_{\rm i,sat}(T)$$
(2.8)

Figure 5 shows the dependency of the molar fraction and the partial vapor pressure of a nonideal mixture compared to the Raoult's and the Henry's law. It is easy to understand from the diagram, the validation limits of each law.



Figure 5: Deviation of the behavior of a non-ideal mixture compared to the Henry and Raoult's law.

The saturation vapor pressure used in Eq. (2.8) can be calculated using the Antoine equation (Eq. (2.9)) [79]:

$$\log_{10}\left(\frac{p_{i,\text{sat}}}{p^0}\right) = A - \frac{B}{C+T}$$
(2.9)

where $p_{i,sat}$ describes the saturation vapor pressure of the water in Pa, p^0 is the reference pressure in Pa, T is the temperature in K and A, B in K and C in K are the material and temperature dependent constants.

The Antoine constants for the saturation vapor pressure of the hydrogen sulfide in bar in a temperature range of 212.8 - 349.5 K are given in Table 5.

The Antoine constants for the saturation vapor pressure of water in Pa for temperatures above 273,15 K are given in Table 6.

Table 5: Specific constants of Antoine equation for hydrogen sulfide, with p_{sat,H_2O} in bar $(p_0 = 1Pa)$ [80].

Temperature T in K	A [-]	B [K]	C [K]
212.8 - 349.5	4.52887	958.587	-0.539

Table 6: Specific constants of Antoine equation for water $(p_0 = 1 \text{ Pa})$ [81].

Temperature T	Saturation vapor pressure	۲ ۱ ۸	Die K	C in K
in K	$p_{{ m sat,H_2O}}$ in Pa	A [-]	BINK	
273.15 - 318.08	611.2 - 9555	10.31549	1794.88	-34.764
318.08 - 394	9555 - 204 045	10.11048	1680.59	-43.932
394 - 647.1	204 045 - 20 728 013	10.09938	1681.00	-43.037

For temperatures below the freezing point of water, its saturation sublimation pressure is given by the Magnus equation after Sonntag in the temperature range of 208,15 K - 273,15 K [82]:

$$p_{\text{sat,H}_20} = 611.2 \cdot \exp\left(\frac{22.46 \cdot T - 6134.949}{T - 0.53}\right)$$
 (2.10)

with the temperature T in K and $p_{\text{sat},\text{H}_2\text{O}}$ in Pa.

In the following section the characteristics of the ionic liquids and especially the physical properties of [EMIM][MeSO₃], which is used in this work, are discussed.

3 Scope of the work

The following work is divided in two parts. The first part refers to the immobilization of the ionic liquids in polymer matrices. The purpose was the development of new polymer-based materials, which could achieve unique and tunable properties in gas purification applications. In this work, an experimental investigation on immobilizing the ionic liquid [EMIM][MeSO₃] in the polymers agar agar and two types of poly(vinyl alcohol) was attempted. First the ionic liquid – polymer mixtures were prepared and characterized. The density is measured with a Hubbard pycnometer as well as the dynamic viscosity using a Falling ball viscosimeter. Furthermore the kinetics of the thermal decomposition of the pure samples (two PVOH types and $[EMIM][MeSO_3]$) and the prepared IL – polymer mixtures were investigated. Discrimination between thermal decomposition and evaporation was achieved by thermogravimetrical analysis (TG) experiments at different temperature rates under nitrogen and helium atmosphere. The kinetics of the thermal decomposition of the ionic liquid $[EMIM][MeSO_3]$, through isothermal TG-experiments, were determined using a model free method known as isoconversional method and afterwards compared to literature data. The kinetics of the thermal decomposition of the other samples were investigated by non-isothermal TG-experiments. Based on the obtained data, a maximum operation temperature for industrial processes and laboratory applications with regard to thermal decomposition was derived for each sample.

The second part of this work concerns the purification of a gas stream from hydrogen sulfide and water vapor. The purification of a gas stream from hydrogen sulfide component was accomplished through an absorption column filled with the dehydrated pure ionic liquid [EM-IM][MeSO₃]. Measurements with gas streams of gases with different hydrogen sulfide contents were accomplished at three different temperatures. The Henry coefficient was determined and compared to common solvents from literature data. The dehydration of humid gas streams was realized using the prepared IL - polymer mixtures as absorbents. Therefor a complete new set-up was build up. Finally the results of these measurements were furthermore compared to the literature data of dehydration using the pure ionic liquid [EMIM][MeSO₃].

4 Experimental method and data analysis

In this chapter the preparation and characterization of the ionogels is presented. In the following, the kinetic computation on thermal analysis data using the isoconversional method and analysis and modeling of TG-experiments is described. Furthermore, the experimental set up and the measurements of the absorption of H_2S in [EMIM][MeSO₃] and H_2O in the prepared ionogels are described.

4.1 Ionogel preparation

The gelling procedure was carried out as following:

The IL [EMIM][MeSO₃] was heated up to 100 °C and stirred concurrently. When the temperature was reached, a well-defined amount of polymer (agar agar, PVOH) was added in small portions. The mixture was stirred at 100 °C until it gets homogenous. After that, the mixture was cooled down. The total water was calculated as the sum of the initial water contents of the polymer sample, the IL sample and, if needed, the additional amount of water.

4.2 Determination of water content in poly(vinyl alcohol)

The examinating samples of poly(vinyl alcohol) are big particles and it is not possible to solubilize them. Thus, a water determination method from Sigma-Aldrich was used: 100ml Methanol and about 7g of sample are weighted and put into an Erlenmeyer flask. The flask has to be tightly closed. The mixture is stirred for a night. The water content of the pure methanol is first determined using the Karl-Fischer Titrator (KF Coulometer 756/831, Metrohm). After that the water content of the mixture was also measured. From the obtained data, the water content of the pure poly(vinyl alcohol) can be calculated.

The same method was used for the determination of the water content in the prepared IL - polymer mixtures (ionogels). The validation of the method was proved by measuring the water content of the ionic liquid – polymer mixtures with thermogravimetrical measurements.

In the next section the density measurements of the samples used in this work are described.

4.3 Density measurements with a Hubbard pycnometer

The densities of the prepared IL - polymer mixtures were measured with a Hubbard pycnometer (Neubert - Glass GbR). The Hubbard pycnometer is suitable for viscous liquids like pastes, vaseline, creams and bitominous compositions. The close-fitting ground glass stopper has a capillary tube NS24/15mm. The relevant characteristics of the pycnometer are shown in Table 7.

Table 7: Characteristics of the Hubbard pycnometer.

Volume	26.025 cm ⁻³
Mass	37.6174 g

At first the pycnometer was validated with glycerin (99 wt%, water free, Grüssing GmbH). The result of the measurement at 31 ± 0.2 °C is shown and compared to the literature value in Table 8.

Table 8: Density of glycerin at 31 ± 0.2°C compared to the literature value [83].

Measured value in g cm ⁻³	Theoretical Value in g cm ⁻³	Error %
1.2518	1.2516 [83]	0.015

The measured densities were used for the calculation of the dynamic viscosities of the IL - polymer mixtures. The dynamic viscosity measurements are described in the next section.

4.4 Viscosity measurements with a Falling Ball Viscosimeter

The dynamic viscosities of the ionic liquid – polymer mixtures were measured with a Falling Ball Viscosimeter (HÖPPLER[®] KF 3.2, RHEOTEST Medingen GmbH) which is based on the measuring principle by Höppler. It operates according to DIN 53015. The falling Ball Viscosimeter is shown in Figure 6.



Figure 6: Falling Ball Viscosimeter (HÖPPLER® KF 3.2, RHEOTEST Medingen GmbH).

In the Falling Ball Viscosimeter the fluid is located in a vertical glass tube with an inclination of 10°. A Thermostat (HAAKE F4) filled with a low viscosity silicone oil $(20 \cdot 10^{-6} \text{ m}^2 \cdot \text{s}^{-1} \text{ at } 25^{\circ}\text{C}$, Polydimethylsiloxane). A sphere of known size and density is allowed to fall through the liquid. The viscosity is calculated by measuring the time, required for the ball, to fall under gravity through a sample-filled inclined tube. The average time of five measurements was taken.

Using Eq. (4.1), the results were converted into a dynamic viscosity value in mPa s.

$$\eta = t \cdot (\rho_1 - \rho_2) \cdot \mathbf{K} \tag{4.1}$$

Where η is the dynamic viscosity in mPa s (cP), t is the time of descent from the top to bottom annular mark in s, ρ_1 is the density of the ball in g cm⁻³, ρ_2 is the density of the fluid in g cm⁻³ and K is the ball constant in mPa cm³ g⁻¹.

The selection of the appropriate ball depends on the viscosity of the liquid. The correct selection of the balls is done according to Table 9 (manufactory specifications).

Ball Number	Minimum fall-	Measuring range in mPa s			
	ing time in s	(upper range at a maximum falling time of 300 s)			
1	60	0,6	•••	5	
2	50	3		30	
3	50	25		250	
4	50	200		4800	
5	30	1250		12500	
6	30	7000		70000	

Table 9: Constants and characteristics of the falling balls.

The constants and characteristics of the falling balls are given in the test certificate for the viscosimeter and are shown in Table 10.

Ball Num-	Diameter	Density ρ_1	Mass	Ball constant K	Ball constant K
ber	in mm	in g cm ³	in g	forward	backward
	(at 20°C)	(at 20°C)		in mPa cm ³ g ⁻¹	in mPa cm ³ g ⁻¹
1	15.802	2.224	4.5944	0.01149	0.01161
2	15.630	2.226	4.4507	0.08143	0.08181
3	15.564	8.145	16.0782	0.1295	0.1297
4	15.104	8.126	14.6599	0.917	0.919
5	14.002	7.720	11.0959	6.721	6.726
6	11.003	7.706	5.3748	34.93	34.94

Table 10: Constants and characteristics of the falling balls.

The Falling Ball Viscosimeter was first validated with H_2O , glycerin and the IL [EMIM][MeSO₃]. The obtained results were compared with the one of the literature data given in Table 11 [84–86]. There were no literature data for the dynamic viscosity of [EMIM][MeSO₃] (95 wt%) at 90°C. For a comparison, dynamic viscosity data for 30°C and 90°C were measured with the capillary viscosimeter AVS 310 from Schott and thermostat DL 20 KP from LAUDA. The densities of this IL, measured at the Chair of Chemical Engineering at the University of Bayreuth were used.

Table 11: Dynamic viscosity validation measurements.

Sample	Temperature	Density	Ball	Viscosity	Literature data
	in °C	in g cm⁻³	number	in mPa s	in mPa s
Water	32 ± 0.4	0.995 [85]	1	0.76216 ± 0.004	0.76417[84]
Glycerin	30 ± 0.3°C	1.252	4	642.76 ± 0.03	612 [86]
	90 ± 0.2°C	1.211	2	21.5±0.2	21.3 [86]
[EMIM][MeSO ₃]	31 ± 0.5°C	1.236	3	111 ± 1.26	122.4
	90 ± 0.5°C	1.198	2	13.54 ± 0.16	13.03
The results of the dynamic viscosity measurements using the Falling Ball Viscosimeter were satisfactorily. As observed from the validation measurements, only a minor deviation from the literature data is recognized. The average error of the validation measurements is about 4%.

In the following the characterization and kinetic computation of the PVOH and the IL - PVOH mixtures using thermogravimetrical analysis is described.

4.5 Thermogravimetrical analysis (TGA)

This chapter describes the methods used for the kinetic computation of the thermal decomposition of the samples from TGA experimental data. At first the kinetic computation using the isoconversional method is described. Furthermore the kinetic computation analyzing and modeling the TG-experimental data is also represented. At last the calculation of the maximum operation temperature of the samples in laboratory and industrial use is mentioned.

4.5.1 Definition of thermogravimetrical analysis

The concept of thermal analysis (TA) is defined in the DIN 51005. Thermal analysis is a general term for measuring methods which measure physical and chemical properties of a substance, a substance mixture or a reaction mixture as a function of temperature or time, while the sample is subjected to a controlled temperature program [87]. From the thermal analysis data it is possible to find out the kinetic parameters of the decomposition of the sample [88,89].

Thermogravimetry is a special measuring method in the field of thermal analysis. The change in mass of a sample is recorded in a defined gas atmosphere during a specified temperaturetime-program [90]. A derived measured variable is the mass loss (TG-Signal) or the rate of mass loss (DTG-Signal, Differential-Thermogravimetry-Signal). The normalization of TG measuring curves or DTG measuring curves is performed using the initial mass. A thermogravimetric measuring instrument is referred to as a thermobalance [33].

4.5.2 Sample preparation and conditioning

For all TGA measurements the program method was first set to a conditioning phase (60 min at 100 °C and after that 60 min at 50 °C) to avoid moisture and then set to the desirable heating rate. The measurements were made under nitrogen and helium atmosphere of 6 l min⁻¹ (NTP). The PVOH samples were crumbled into smaller particles in order to get homogenous sample for the TG-measurements. The particles size of the samples for the measurements was tried to be kept constant.

4.5.3 Discrimination between thermal decomposition and evaporation during a TG-experiment

Every sample was first measured under nitrogen and helium atmosphere, at the same temperature conditions. No differences at the normalized rate of mass loss in the whole temperature range, means that only a pure thermal decomposition takes place. If differences at the curve are recognized, a pure or a partial evaporation takes place [33].

Furthermore the calculation of the kinetic parameters of the ionic liquid [EMIM][MeSO₃] using the isoconversional method is described.

4.5.4 The isoconversional Method

The isoconversional methods are used for the description of the kinetics from thermal analysis data. The activation energy is determined as a function of conversion without assuming or determining any particular form of the reaction model. This is the advantage of the method and the reason why this method is frequently called "model free" method. Although the reaction model has to be considered and identified because the rate of conversion depends on the function f(x) [89,91–93]. Using thermogravimetric analysis data (TGA) from 3-5 runs at different heating rates or a series of runs at different constant temperatures, a correlation of the kinetic parameters may be obtained [89,91].

The z(X) plot and the determination of the kinetic model

Kinetics deals with measurement and parameterization of the process rates. The process rate can be a function of three parameters, the temperature T, the extent of conversion X which is represented by the reaction model f(X) and the pressure p:

$$\frac{\mathrm{d}X}{\mathrm{d}t} = k(T)f(X)h(p) \,. \tag{4.2}$$

In most of the kinetic computational methods used in thermal analysis, the pressure dependence is ignored. The majority of isoconversional kinetic methods consider the rate to be a function of two variables, temperature T and conversion X [89]

$$\frac{\mathrm{d}X}{\mathrm{d}t} = k(T)f(X) \,. \tag{4.3}$$

The dependency of the process on temperature is parameterized through the Arrhenius equation

$$k(T) = k_0 \exp\left(-\frac{E_a}{RT}\right) \tag{4.4}$$

where k_0 is the pre-exponential factor, E_a the activation energy and R is the universal gas constant. The purpose is to determine a kinetic triplet k_0 in s⁻¹, E_a in J mol⁻¹, f(X) that describes the process. Integration of Eq. (4.3) leads to the integral form of the model reaction:

$$g(X) = \int \frac{\mathrm{d}X}{f(X)} = k_0 \int_0^t \exp\left(-\frac{E_a}{RT}\right) \mathrm{d}t = \frac{k_0}{\beta} \int_0^T \exp\left(-\frac{E_a}{RT}\right) \mathrm{d}T$$
or $g(X) = -\ln(1-X) = \frac{k_0}{\beta} \int_0^T \exp\left(-\frac{E_a}{RT}\right) \mathrm{d}T$
(4.5)

where β is the heating rate in K s⁻¹.

The temperature integral of Eq. (4.5) can be replaced with various approximations $\pi(\kappa)$ as follows:

$$g(X) = \frac{k_0 E_a}{\beta R} \exp(-\kappa) \left[\frac{\pi(\kappa)}{\kappa} \right] \quad \text{with } \kappa = E_a / RT.$$
(4.6)

Combining the differential and integral forms of the reaction models derives the z(X) master plot. From Eq. (4.3) and Eq. (4.6) follows the z(X) function as:

$$z(X) = f(X)g(X) = \left(\frac{\mathrm{d}X}{\mathrm{d}t}\right)_X T_X^2 \left[\frac{\pi(\kappa)}{\beta T_X}\right]. \tag{4.7}$$

It has been established that the term in the brackets of Eq. (4.7) has a negligible effect on the shape of the function z(X). Thus, the value of z(X) for each value of conversion can be determined by multiplying the experimental values of $\left(\frac{dX}{dt}\right)_X$ and T_X^2 [89].

The selection of the appropriate model is a very important step in model fitting. In Table 12 some of the kinetic reaction models are shown.

Reaction Model	Code	<i>f(X)</i>	g(X)
Mampel (First order)	F1	1-X	-ln(1-X)
Contracting sphere	R3	3(1- <i>X</i>) ^{2/3}	1-(1- <i>X</i>) ^{1/3}
Contracting cylinder	R2	2(1-X) ^{1/2}	1-(1- <i>X</i>) ^{1/2}
Two dimension diffusion	D2	[-ln(1-X)] ⁻¹	(1-X)ln(1-X)+X

Table 12: Kinetic reaction models.

The experimental data are determined from non-isothermal thermogravimetric analysis data. The results of the experimental values of z(X) will be plotted as a function of the conversion and compared against the theoretical z(X) master plots. A suitable model is identified as the best match between the experimental and the theoretical z(X) master plots. Figure 7 shows the theoretical master plots for the reaction models listed in Table 12.



Figure 7: Theoretical z(X) master plots for the reaction models listed in Table 12.

Activation energy computation and pre-exponential factor

. . .

Isoconversional methods take their origin in the isoconversional principle that states that the reaction rate at constant extent of conversion is only a function of temperature [89]. The isoconversional principle lays a foundation for a large number of isoconversional computational methods that can generally be split in two categories, differential and integral. In this work the method of Friedman is used which is the most common differential isoconversional method [89,94]. The method is based on Eq. (4.8):

$$\ln\left(\frac{\mathrm{d}X}{\mathrm{d}t}\right)_{X} = \ln\left[f(X)k_{0_{X}}\right] - \frac{E_{a}}{\mathrm{R}T}.$$
(4.8)

The dependence only from the temperature can be easily demonstrated by taking the logarithmic derivate of the reaction rate Eq. (4.3) at a constant conversion:

$$\left[\frac{\partial \ln\left(\frac{dX}{dt}\right)}{\partial T^{-1}}\right]_{X} = \left[\frac{\partial \ln k(T)}{\partial T^{-1}}\right]_{X} + \left[\frac{\partial \ln f(X)}{\partial T^{-1}}\right]_{X}.$$
(4.9)

In this case f(X) is constant because of X = const., so that the second term in the right hand side of Eq. (4.9) equals zero. Thus:

$$\left[\frac{\partial \ln\left(\frac{\mathrm{d}X}{\mathrm{d}t}\right)}{\partial T^{-1}}\right]_{X} = -\frac{E_{a}}{\mathrm{R}}.$$
(4.10)

The activation energy can be evaluated from the slope without assuming any particular form of the model reaction. To obtain the temperature dependence of the isoconversional rate, a series of runs at different constant temperatures have to be performed. For every temperature and every conversion, a process rate is calculated from the average term of the process rate for $X \pm 0.01$. An E_a value in a range of X=0.2-0.7 with a step of 0.1 for each temperature is determined. For every conversion the activation energy is estimated from the linear fit of Eq. (4.10). The average of them results the activation energy of the sample.

The intercept of the plot $\ln\left(\frac{dX}{dt}\right)_X$ and T^1 of Eq. (4.8) represents the $\ln[f(X)k_{0X}]$. The preexponential factor depends on the reaction model. For every conversion a pre-exponential factor is calculated. The fit on the logarithmic Arrhenius plot of all conversions with fixed activation energy results the pre-exponential factor. The above described procedure was used to analyze the thermal decomposition of the pure IL [EMIM][MeSO₃]. This method was compared to the simple method, developed at the Chair of Chemical Engineering of the University of Bayreuth, described in the following section [33].

4.5.5 Analysis and modeling of TG-experiments at ambient pressure and constant heating rate

In the following the rate of mass loss during a non-isothermal TG-experiment is formally described by a first order kinetics. This assumption is based on two observations.

- During non-isothermal TG-experiments, the rate mass loss caused by thermal decomposition only depends on the initial mass.
- When only thermal decomposition takes place during a non-isothermal TGexperiment, the mass signal shows an inflection point. This could not be described with a zero order kinetics [32].

Based on this assumptions, the normalized rate of mass loss due to thermal decomposition for a component i during a thermogravimetrical measurement is expressed by:

$$-\frac{\mathrm{d}m_{\mathrm{i}}}{\mathrm{d}t} = k(T) m_{\mathrm{i}} \quad \text{or} \quad -\frac{1}{m_{0}} \frac{\mathrm{d}m_{\mathrm{i}}}{\mathrm{d}t} = k(T) \frac{m_{\mathrm{i}}}{m_{0}}.$$
 (4.11)

where m_0 is the initial mass and m_i the residual mass.

The dependence of the rate constant of the thermal decomposition from the temperature k(T) is given by the Arrhenius equation (Eq. (4.4)).

Introducing the conversion *X*:

$$X_{\rm i} = \frac{m_0 - m_{\rm i}}{m_0} = 1 - \frac{m_{\rm i}}{m_0} \Rightarrow \frac{m_{\rm i}}{m_0} = 1 - X_{\rm i}$$
 (4.12)

and differentiation of Eq. (4.12):

$$\frac{\mathrm{d}m_{\mathrm{i}}}{\mathrm{d}X_{\mathrm{i}}} = -m_0 \quad \Rightarrow \quad \mathrm{d}m_{\mathrm{i}} = -m_0 \mathrm{d}X_{\mathrm{i}}. \tag{4.13}$$

Eq. (4.11) turns into:

$$\frac{dX_{i}}{dt} = k(T)(1 - X_{i}).$$
(4.14)

The experimental data were fitted by Eq. (4.14) adjusting the parameters k_0 and E_a . In the following the maximum operation temperature calculated from the thermal decomposition kinetic parameters is described.

4.5.6 Definition of the maximum operation temperature with regard to the thermal decomposition

In the case that the measured sample has a pure thermal decomposition, this means that the evaporation is negligible, the conversion due to thermal decomposition can be calculated through Eq. (4.15) using kinetic data obtained from TG-measurements. This equation describes the conversion at a given temperature within a certain time interval

$$X = 1 - \exp(-k(T) \cdot t).$$
(4.15)

Once the parameters of the kinetics of the thermal decomposition are known, it is possible to define a reliable maximum operation temperature for any application. For an industrial process in this work, a loss of 1% per year and for laboratory applications 1% per month (30 days) is suggested [33]. Rearrangement of Eq. (4.15) leads to:

$$T_{\max} = \frac{E_{a}}{R} \cdot (\ln(t) + \ln(k_{0}) - \ln(-\ln(1 - X)))^{-1}.$$
(4.16)

After characterizing the used samples, two different vapor liquid equilibria were studied: the H_2S - [EMIM][MeSO₃] and the water - ionogel vapor liquid equilibrium. In the following the set-up and analysis of the absorption of H_2S in the ionic liquid [EMIM][MeSO₃] and the dehydration of a gas stream from the water component using the [EMIM][MeSO₃] and the prepared ionogels are presented.

4.6 H₂S Absorption

During absorption, a gas component is selectively dissolved by contact with a fluid in which the component is soluble [64]. In this case, scrubbing a gas stream from H_2S using the ionic liquid [EMIM][MeSO₃] as absorbent was accomplished. In the following sections the experimental set-up and the data evaluation is presented.

4.6.1 Experimental Set-up

The most important parts of the set-up are the absorption column, the mass flow controllers and the gas analyzer. The apparatus is shown schematically in Figure 8 and Figure 9.



Figure 8: Schematic set-up for the H₂S absorption in [EMIM][MeSO₃].



Figure 9: Set-up for the H₂S absorption in [EMIM][MeSO₃].

Absorption Column

The absorption column is a shell side heat exchanger with inner diameter 2.9 cm and outer diameter 4.8 cm. Water heats up with a thermostat (RKS 20, Lauda Company). The column is filled until height of 29 cm with column packing balls of 6mm diameter. The gas is entered into the column, flows through the IL [EMIM][MeSO₃] and then continuous to the gas analyzer (NGA 2000MLT 3, Emerson Process Management).

The [EMIM][MeSO₃] was dried with a rotary evaporator (Hei-VAP Value, Heidolpf with the PC 510 NT, Vacuubrand) before usage. The initial concentration of water in the ionic liquid was measured by Karl Fisher Titration (KF Coulometer 756/831, Metrohm) and equals 0.36 wt %. The column was filled with 94.56 g of [EMIM][MeSO₃].

Gas Analyzer

The gas that is fed to the column is a mixture of 1.5 Vol.-% H_2S/N_2 gas which could be further diluted with N_2 . The volume of the two flows is shown in Table 13. The gas analyzer (NGA 2000MLT 3, Emerson Process Management) measures the concentration of H_2S . The measuring channel of the gas analyzer has to be calibrated before use. There must be set a span calibration before the first use and a zero gas calibration before every measurement. For the span calibration various concentrations of H_2S were generated by diluting the 1.5 Vol.-% H_2S/N_2 gas with nitrogen as shown in Table 13. The zero gas calibration is performed with nitrogen flow. Thereafter, a linearization of the measuring channel was performed. Two Mass Flow Controllers (Model 5850 TR Series, BROOKS Instrument) were used for the flow measurement and flow control of the gases. The flows were measured and then converted to Standard Temperature and Pressure (STP) conditions (T = 0 °C, p = 1.01325 bar).

	N ₂		H_2S/N_2	
ppm ± 15 ppm	MFC ± 0.1%	l h ⁻¹ ± 1% (STP)	MFC± 0.1%	l h ⁻¹ ± 1% (STP)
550	84.8	157.7	5.2	6.0
800	86.0	160.0	8.1	9.0
1375	59.2	109.0	10.0	11.0
1500	54.0	99.0	10.0	11.0
1813	44.0	80.0	10.0	11.0
2000	39.5	71.5	10.0	11.0
2200	35.6	64.0	10.0	11.0
3300	22.4	39.0	10.0	11.0
4024	17.7	30.0	10.0	11.0
6250	10.0	15.4	10.0	11.0
9622	21.9	38.0	66.0	68.0

 Table 13:
 Volume of diluted H₂S with nitrogen gas flows for various concentrations.

After that, the linearization has been checked using two validation measurements with calibration gases. The results are shown in Table 14 and proof the validity of the performed calibration.

Table 14: Validation using calibration gases.

Set point in ppm	Actual Value in ppm
1024 ± 20.48	1050 ± 15
100.6 ± 2	127 ± 15

4.6.2 Absorption of H₂S in [EMIM][MeSO₃]

Absorption measurements at three different temperatures, 20°C, 30°C and 50°C and H_2S/N_2 concentrations of 550, 2000, 4000 and 8000 ppm were performed in the absorption apparatus shown in Figure 8, using [EMIM][MeSO₃] as absorbent. Each absorption experiment was conducted as follows:

After reaching a stable temperature of the ionic liquid in the column, the mass flow controllers both nitrogen and hydrogen sulfide are set on a set point. The volume flows were checked at the beginning and the end of the measurement to certify their stability and converted in NTP conditions (T = 20 °C, p = 1.01325 bar). At first the inlet, H₂S concentration of the column, was measured using the bypass. After the concentration signal didn't vary anymore, the gas stream was sent through the column and then to the gas analyzer. The IL absorbs H₂S until the concentration at the gas analyzer returns to its initial concentration. In order to check whether the inlet H₂S concentration has changed during the experiment, the gas was again passed through the bypass. At last the gas flows again through the bypass, the H₂S valve turns off and the gas analyzer shows zero ppm while he receives only nitrogen. Figure 10 shows an absorption example for a 2100 ppm H₂S/N₂ mixture at a temperature of 32 °C.



Figure 10: Example of an absorption experiment (2100 ppm H_2S/N_2 , T = 32 °C).

4.6.3 Desorption of H₂S from [EMIM][MeSO₃]

Desorption measurements of the hydrogen sulfide from the IL [EMIM][MeSO₃] were conducted, to verify that the gas that is absorbed in the ionic liquid can also be desorbed. Therefor the loaded IL was stripped with pure nitrogen at the same temperature as for the absorption. In order to verify if the whole H₂S amount was desorbed, the column temperature was increased until almost all H₂S has desorbed. Figure 11 shows a desorption example for a 2100 ppm H₂S/N₂ flow mixture at a temperature of 32 °C.



Figure 11: Example of a desorption experiment (2100 ppm H_2S/N_2 , T = 32 °C).

In order to conduct gas dehydration experiments with ionogels, a new set-up was built up. This dehydration set-up is described in detail in the following section.

4.7 Gas dehydration using ionogels

In this section the experimental set-up and analysis of the gas dehydration plant using ionic liquid – polymer mixtures are described. Furthermore, the most important parts of the experimental apparatus and the data evaluation are presented.

4.7.1 Experimental Set-up

Figure 12 shows the schematic set-up for gas dehydration with using ionic liquid – polymer mixtures. The nitrogen flow is controlled by a mass flow controller (Model 5850 TR Series, BROOKS Instrument) and can be either satured with moisture or feed directly in the absorption apparatus. All tubes are made from stainless steel (3mm diameter) to prevent corrosion. The absorption apparatus and its most important parts are shown in Figure 13.



Figure 12: Schematic set-up for the H₂O absorption in polymer mixtures with the additional part of the set-up for dilution of the saturated gas stream (dashed frame).



Figure 13: The absorption plant.

Saturator

The saturator is a shell side heat exchanger. The temperature is controlled using a thermostat (Immersion thermostat A 100, LAUDA). Its diameter is 11 cm and the height 30cm. The saturator is filled with 6x6 mm Rasching rings and water until the 3/4 of its high. When the gas flows through the water, having a sufficient contact time, the dew point of the gas corresponds to the temperature of the water.

In order to achieve lower dew points, an additional piping with two dosing valves was added to the apparatus as shown in Figure 12 (dashed frame). With this extension a dilution of the saturated gas stream with nitrogen stream can be achieved. Thus, dew points under 14°C could be obtained.

Absorber

The absorber is shown in Figure 14. It consists of three parts, the top, the bottom and the heating jacket. The bottom part of the absorber has a recess ($A_{abs.}$ = 24,78 cm²) where the absorbent is filled in. A temperature sensor is placed in the absorber. The gas in and outlet of the absorber are located at the top of the absorber.



Figure 14: Upper and lower part of the absorption column.

The column is screwed sturdily between a fitment to avoid gas loss. The absorber is placed in a heating jacket (maximum temperature application 250°C). The moisture content of the gas streams were detected by tow humidity sensors described in the following part.

To certify the stability of the temperature through all the absorbent placement of absorption apparatus, a temperature profile along the recess was made. The temperature indicator was put from the begging of the recess at the temperature indicators guideway to the end of it (distance of 24 cm). The temperature was measured from the beginning (x = 0 cm) to the end (x = 24cm) every 2 cm. The temperature profile was made for temperatures of 30 °C, 40 °C, 60 °C, 80 °C and 90 °C and at three different normalized (STP) volume flows of 44 l h⁻¹, 88 l h⁻¹ and 130 l h⁻¹. The temperature profiles at all temperature and volume flows were stable with a maximum deviation of 0.2 °C. The temperature profile of the 44 l h⁻¹ volume flow is exemplarily shown in Figure 15.



Figure 15: Temperature profile of the absorption apparatus at a normalized volume flow of $44 \mid h^{-1}$.

Humidity sensors

Two humidity sensors (HYT-221, Hygrosens), one at the absorber entrance and one at the absorber outlet, were used in this dehydration plant. The sensor is a capacitive polymer humidity sensor with intergraded signal flow. The signal processing integral in the sensor, completely processes the measured data and directly delivers the physical parameters of relative humidity (rH) and temperature over the I²C compatible interface as digital values. The module is first precisely calibrated. The most important technical data of the HYT-221, Hygrosens are shown in Table 15.

	Humidity measuring range	0-100% rH	
Humidity measurement	Humidity accuracy	±1.8% rH (at 0-80% rH)	
	Response time	<12 sec with membrane filter	
	Temperature measuring range	-40 - 125°C	
lemperature measure- ment	Temperature accuracy	±0.2 K (at 0-60°C)	
	Response time	<12 sec with filter	
	Operating voltage	2.7-5.5 V	
Operating data	Application temperature	-40 – 125°C	
	Humidity application range	0 – 100% rH	

Table 13. Temperature campration into or the temperature multators	Table 15:	Temperature	calibration	fits of the	temperature indicators
---	-----------	-------------	-------------	-------------	------------------------

For the adjustment, monitoring and recording of the operating parameters and measured values, a separate monitoring program in Visual Basic 2010 was written [95]. In the following section the absorption process is described and an exemplary experiment is shown.

4.7.2 Absorption of water in the polymer mixtures

Absorption measurements were accomplished at different dew points of the feed gas and absorbent temperatures. Each absorption experiment was conducted with the apparatus shown in Figure 12 as follows:

After the absorbent in the absorption apparatus and the saturator has reached a stable temperature, the mass flow controller of nitrogen was set on a set point. The volume flows were checked flowing bypass of the saturator and through the absorption apparatus, through the saturator and bypass the absorption apparatus and through the saturator and then throw the absorption apparatus. These volume flow measurements were made at the beginning and the end of the experiments to certify the stability of the flow and converted to STP conditions (T = 0 °C, p = 1.013 bar). Starting the measurement, the gas flow passes the saturator and bypasses the absorber until the dew point doesn't vary anymore. After the signal didn't vary anymore, the gas stream was passed through the absorption apparatus. The absorbent absorber absorber apparatus sees no humidity. At the end of the absorption the absorber the absorber and the humidity and dew point of the sensor after the apparatus is again at its initial values.

Figure 16 shows an experiment example of an absorption having as absorbent the 9,8 wt% Mowiol 56-98 in $[EMIM][MeSO_3]$ mixture with an absorber temperature of 43 °C and a dew point of the feed gas of 17 °C.



Figure 16: Example of a water absorption experiment with 9,8 wt% Mowiol 56-98 in [EMIM][MeSO₃] mixture with an absorber temperature of 43 °C and dew point of the feed gas of 17 °C.

In the following chapter, the results of this work are presented and furthermore discussed. The first part of chapter 5 concerns the material characterization. In the second part the absorption measurement of H_2S and water are presented.

5 Results and discussion

The results of the measurements are furthermore discussed and compared to the literature data. First the results of the density and viscosity measurements as well as the kinetic of the thermal decomposition of [EMIM][MeSO₃], the two PVOH types and PVOH-[EMIM][MeSO₃] mixtures are presented. In the following the results of the absorption of H₂S in pure [EM-IM][MeSO₃] are presented. Last but not least, the results of the gas dehydration using the prepared ionogels are shown and discussed.

5.1 Agar agar Kobe I - [EMIM][MeSO₃] mixtures

At first the agar agar Kobe I and the [EMIM][MeSO₃] were dried with the rotary evaporator (Hei-VAP Value, Heidolpf with the PC 510 NT, Vacuubrand) at 60 - 70 °C and 90 °C respectively. The water content of each sample was determined by the Karl Fisher Titration (KF Coulometer 756/831, Metrohm). The water content of agar agar before and after the evaporation was about 16 wt % water in both measurements, which means that it was not possible to remove the water from the agar agar powder in this way. The [EMIM][MeSO₃] has only 0.36 wt % water. So the gels will always have a relatively high amount of water.

A series of mixtures at different agar agar - [EMIM][MeSO₃] - water ratio were produced. The water couldn't be ignored because of its high concentration in the agar agar. However most of the mixtures have additional water. It was figured out that an amount of water is necessary for the better solubilization of agar agar.

The results were mixtures of different viscosities. The mixtures were divided as liquids (low viscosity), pastes (high viscosity) or gels (solid). Figure 17 shows the ternary plot of agar agar Kobe I, [EMIM][MeSO₃] and water. The grey line represents the lower limit of the water content because of the irremovable amount of water in the agar agar Kobe I. As a consequence, mixtures with water contents bellow 16 wt% can't be prepared. It is also impossible to prepare a gel with a small amount of water. There have to be at least 20-25 wt % water to become a gel.





The necessity of high water content in the gel is not desirable. It was also noticed that some of the gels which had a high amount of water became moldy after 2-3 months as shown in Figure 18. For this reason the idea to use agar agar as gelator was rejected and gels using PVOH were tried out.



Figure 18: Gels with a high amount of water became moldy after 2-3 months.

5.2 PVOH - [EMIM][MeSO₃] mixtures

From the two PVOH types, six mixtures were prepared. The concentration of each was calculated as follows. For every mixture, 60 ml [EMIM][MeSO₃] were weighted and then varying the PVOH quantity, mixtures with different PVOH concentration were prepared. For the concentration determination, the following has to be noticed. These mixtures have also a small part of water. The water of the Mowiol was 0.2 wt% and of the [EMIM][MeSO₃] 0.3 wt%. The prepared mixtures are shown in Table 16. Their water content is measured as described in Section 4.2.

PVOH type	Concentration of PVOH	Viscosity
	in wt%	at RT
Mowiol 56-98	4.8	low
Mowiol 56-98	5.0	low
Mowiol 56-98	9.8	high
Mowiol 56-98	15	solid
Mowiol 40-88	5.2	low
Mowiol 40-88	9.9	high

Table 16: Mowiol 56-98- [EMIM][MeSO₃] and Mowiol 40-88 - [EMIM][MeSO₃] mixtures.

However the approximate upper concentration limits of both PVOH types in water was 12 wt% [48], mixtures of 15 wt% Mowiol in[EMIM][MeSO₃] were also tried out. The results were mixtures full of bubbles because of their high viscosity that didn't let them stir correctly.

Although, obviously some of these mixtures are pastes and not gels the term "ionogel" is used in the following course of the work in parts.

The above mentioned ionogels were characterized and used as absorbents for the gas dehydration. In the following the density measurements of the prepared ionogels are presented and discussed.

5.3 Density measurements of IL-polymer mixtures

The density measurements were carried out using a Hubbard pycnometer which is suitable for pastes like vaseline, creams and bituminous masses. All densities were measured from 30 °C to 90°C in steps of 10°C.

In Figure 19 the results of the density measurements of the ionogels are presented and compared to the density of the [EMIM][MeSO₃]. The densities of the IL [EMIM][MeSO₃] were already measured at the Chair of Chemical Engineering at the University of Bayreuth.



Figure 19: Densities of the prepared IL – polymer mixtures compared to the pure ionic liquid [EMIM][MeSO₃].

It is easy to recognize that the densities shows same trend like the IL sample. All curves are almost parallel to the density of the [EMIM][MeSO₃]. It was expected that the PVOH - [EM-IM][MeSO₃] ionogels would have higher densities than the pure ionic liquid. An explanation for this deviation could be the water content of the ionogels. The mixtures are absorbing water from the environment during their storage and the filling into the pycnometer. Unfortunately the water content was measured a few days after the density measurements. The results of the measurements are shown in Table 17. Even though the obtained density data are reliable, the observed differences between the neat IL and the polymer mixtures are rather small.

Table 17: Mowiol 56-98 - [EMIM][MeSO₃] and Mowiol 40-88 - [EMIM][MeSO₃] mixtures.

Sample	Water content in mol%
4.8 wt% Mowiol 56-98 in [EMIM][MeSO ₃]	32
5.0 wt% Mowiol 56-98 in [EMIM][MeSO ₃]	49
9.8 wt% Mowiol 56-98 in [EMIM][MeSO ₃]	59
5.2 wt% Mowiol 40-88 in [EMIM][MeSO ₃]	18
9.9 wt% Mowiol 40-88 in [EMIM][MeSO ₃]	48

The bubbles and the high viscosity of the 15wt% Mowiol 56-98 - [EMIM][MeSO₃] ionogel didn't make it possible to measure its density either the viscosity. In the following the results of the dynamic viscosity measurements are presented.

5.4 Viscosity measurement of ionic liquid - polymer mixtures with the Falling Ball Viscosimeter

At first the IL – polymer mixtures were put in a water bath to take a liquid form again. Then it was able to fill them into the glass tube of the viscosimeter. The dynamic viscosity measurements were conducted at 30°C, 60°C and 90°C. The average falling time of five forward and five backward measurements were taken. The Mowiol 56-98 - [EMIM][MeSO₃] ionogels and Mowiol 40-88 - [EMIM][MeSO₃] ionogels were measured. The results are shown in Table 18.

Sample	Water con-	Temperature	Density	Ball	Viscosity
	tent in	in °C ±0.3	in g cm⁻³	number	in mPa s
	mol%				
4.8 wt% Mowiol 56-98 in		32	1.233	6	25838 ± 419
[EMIM][MeSO ₃]	32	61	1.215	5	5012 ± 184
		90	1.196	4	2054 ± 107
5.0 wt% Mowiol 56-98 in		30	1.233	6	13424 ± 243
[EMIM][MeSO ₃]	49	60	1.215	5	1371 ± 10
		90	1.196	4	860 ± 5
9.8 wt% Mowiol 56-98 in	59	90	1.203	6	14796± 323
[EMIM][MeSO ₃]					
5.2 wt% Mowiol 40-88 in		30.7	1.231	6	23704 ± 216
[EMIM][MeSO ₃]	18	59.6	1.213	5	4253 ± 13
		90.3	1.199	4	1173 ± 3
9.9 wt% Mowiol 40-88 in [EMIM][MeSO₃]	48	90	1.192	6	10741± 90

 Table 18:
 Dynamic viscosity of PVOH - [EMIM][MeSO₃] mixtures.

The viscosity of the almost 10 wt% PVOH in [EMIM][MeSO₃] ionogels could be measured only at 90°C. At the other two temperatures, the time of the ball falling exceeded the maximum falling time.

The viscosities are decreasing as the temperature rises and as the PVOH concentration rises. It was figured out that the water content of the ionogels is also an important parameter affecting the viscosity measurements and leads to a decrease of the viscosity. The given water contents were also measured a few days after the viscosity measurement and are therefor not reliable.

In conclusion, the water content of the ionogels has to be considered for the density and viscosity measurements. Before and after every measurement, the water content has to be determined. The ionogels have to be stored in a tight closed bottle, so that no water can be absorbed at its storage. In the following section the characterization of the ionic liquid [EM-IM][MeSO₃] is presented.

5.5 Characterization of the IL [EMIM][MeSO₃] using thermogravimetric analysis data

In the next section the ionic liquid [EMIM][MeSO₃], is characterized using thermogravimetrical analysis data. At first determined if evaporation has to be taken into account. Furthermore the kinetic parameters of the thermal decomposition of the ionic liquid [EMIM][MeSO₃] using the isoconversional method (section 4.5.4) and the maximum operation temperature (Section 4.5.6) are calculated and discussed.

5.5.1 Discrimination between thermal decomposition and evaporation during the TGexperiments with the ionic liquid [EMIM][MeSO₃]

Discrimination between thermal decomposition and evaporation due to the TG-experimental data was carried out. Figure 20 shows the thermogravimetric measurement of the [EM-IM][MeSO₃] under nitrogen (N₂) and helium (He) atmosphere of 6 l h⁻¹ (NTP) and temperature rate of 2 K min⁻¹ in glass pans. No significant deviation is recognized at the two measurements. This confirms the assumption of pure thermal decomposition of the ionic liquid during the TG-experiments.



Figure 20: TG-experiments of $[EMIM][MeSO_3]$ under N₂ and He atmosphere (HR = 2 K min⁻¹, 6 l h⁻¹ NTP).

5.5.2 Kinetic of thermal decomposition of [EMIM][MeSO₃]

The kinetic computation of the ionic liquid [EMIM][MeSO₃] was made using the differential isoconversional method of Friedman [49,89,94] (section 4.5.4). As mentioned in section 5.5.1, TG-experiments were made at a temperature rate of 2 K min⁻¹ in helium and hydrogen atmosphere (6 I h⁻¹ NTP) in glass pans. No differences at the normalized mass loss rates were noticed. Thus, the mass loss signal can be referred to a pure thermal decomposition of the IL and evaporation can be neglected. A *z*(*X*) plot was plotted as a function of the conversion *X* according to Eq. (4.7) and compared to the theoretical *z*(*X*) master plots. The comparison is shown in Figure 21. The thermal decomposition of [EMIM][MeSO₃] follows the 1st order reaction model over a wide range of conversion (< 0,8).



Figure 21: Comparison of the theoretical 1^{st} order reaction model and the TGA measures of [EMIM][MeSO₃] under He and N₂ atmosphere (HR = 2 K min⁻¹, 6 I h⁻¹ NTP).

Furthermore isothermal TGA measurements at 8 different temperatures between 255-325 °C were conducted. These temperatures were chosen because the thermal decomposition of [EMIM][MeSO₃] becomes measurable at about 255 °C.

As described in section 4.5.4, for every temperature and every conversion, the logarithmic derivate of the reaction rate $\ln \left(\frac{dX}{dt}\right)_X$ is calculated from the average term of the conversion for X ± 0.01. The $\ln \left(\frac{dX}{dt}\right)_X$ of every conversion at the different temperatures vs T⁻¹ plot was made according to Eq. (4.8).

The intercept of the plot $\ln\left(\frac{dX}{dt}\right)_X$ and T^1 of Eq. (4.8) represents the $\ln[f(X)k_{0_X}]$. The preexponential factor depends on the reaction model, i.e. in this case 1^{st} order reaction model (see section 5.5.4). For every conversion a pre-exponential factor is calculated.

For example, the calculation for X = 0.6 is explained: From every isothermal measurements, the logarithmic derivate of the reaction rate $\ln \left(\frac{dX}{dt}\right)_{X=0.6\pm0.01}$ is calculated as the average of

the conversion from X = 0.59 to X = 0.61. The $\ln\left(\frac{dX}{dt}\right)_{X=0.6\pm0.01}$ to the T^{-1} plot according to Eq. (4.8) was made as shown in Figure 22. The activation energy from the slope and the pre-exponential factor were calculated for this conversion.



Figure 22: The $\ln\left(\frac{dX}{dt}\right)_X$ to T⁻¹ plot for X= 0.6 for the eight isothermal TG-experiments (6 | h⁻¹ N₂ NTP).

These steps were done for all conversions. The results were six activation energies and preexponential factors. Figure 23 shows the calculated activation energies.



Figure 23: The calculated activation energies for every conversion obtained from the isoconversional method.

In order to get an average pre-exponential factor, the six kinetic data sets were taken and plotted in an Arrhenius plot (see Figure 24). Via linear regression the average value as obtained using the before determined average activation energy of 137 kJ mol⁻¹. The linear fit of the Arrhenius plots of all calculated conversions results the pre-exponential factor. The activation energy of the ionic liquid [EMIM][MeSO₃], calculated with the isoconversional method is 137 kJ mol⁻¹ and the pre-exponential factor is $6.2 \cdot 10^8 \text{ s}^{-1}$.



Figure 24: Arrhenius plot of kinetic parameters of [EMIM][MeSO₃] for conversions 0.2 to 0.6 with step 0.1.

The result of the isoconversional method was compared to the results the TG-measurements $(E_a = 189 \text{ kJ mol}^{-1}, k_0 = 3.9 \cdot 10^{13} \text{ s}^{-1})$, the isothermal magnetic suspension balance (MSB) measurements at N₂ (1 bar) and different temperatures ($E_a = 142 \text{ kJ mol}^{-1}$, $k_0 = 8.5 \cdot 10^7 \text{ s}^{-1}$) and the recommended data as the average of the TG- and MSB- experiments ($E_a = 199 \text{ kJ mol}^{-1}$, $k_0 = 2.9 \cdot 10^{14} \text{ s}^{-1}$) given in the literature [33]. The comparison is shown in Figure 25. The starting and ending points of each line indicated the temperature range in which the given kinetic dataset is valid. Taking the different areas of validity into account, the results are very satisfactorily.



Figure 25: Rate constant of thermal decomposition of [EMIM][MeSO₃] calculated with the isoconversional method compared to the TGA and MSB measurements and the recommended data in the literature [33].The starting and ending points of each line indicate the range in which the given kinetic datasets are valid.

Nevertheless the computation of the kinetic parameters using the isoconversional method took considerable time without having any advantage compared to the other TGA method (analysis and modeling of TG-experimental data). The results obtained by the two different methods are within the errors equal to each other. However the TGA method is a quick and confidant method. For this reason the computation of the kinetic parameters of all further samples will be accomplished with the TGA method.

The maximum operating temperature was calculated using Eq. (4.15) with the already known kinetic data from the literature [33]. For an industrial process, losses of 1% per year and for laboratory applications 1% per month (30 days) were determined. The maximum operating temperature for an industrial process is about 181 °C and for laboratory application 160 °C.

In the following section the characterization of the two PVOH types are presented. Furthermore the results of the kinetic of their thermal decomposition with the TGA method (section 4.5.5) are shown.

5.6 Characterization of Mowiol 56-98 and Mowiol 40-88

In this section, the characterization of Mowiol 56-98 and Mowiol 40-88 with TG-measurements is presented. The dependence on the crucibles materials as well as on the initial mass of the measured samples is investigated. Furthermore the kinetic parameters of the thermal decomposition of the pure polymers were calculated analyzing and modeling the TG-experimental data (section 4.5.5) obtained from TG-experiments.

5.6.1 Influence of the crucible material during TG-experiments

At first it was examined if the use of quartz glass or aluminum crucible has an influence on the thermal degradation of the PVOH. As shown in Figure 26 the crucible material doesn't influence the results. Although it affects the measurements of the pure IL [EMIM][MeSO₃]. For this reason for all following TG-measurements only glass crucible were used in order to make the different measurements comparable.



Figure 26: TG-experiments with Mowiol 56-98 using quartz glass and aluminum crucible and almost the same initial mass of about 6 mg (HR = 2 K min⁻¹, 6 l h⁻¹ N₂ NTP).

5.6.2 Dependence of the TG-signal on the initial mass of the sample

An influence on the rate of mass loss by varying the initial mass of the samples was not observed. Only at high weights a minor influence was noticed as shown in Figure 27. Although another reason could also be the different density of the small "fixed bed" of the PVOH in every measured sample. The samples were tried to be taken with the same particle size. The samples for the kinetic computation had an initial weight of 6 \pm 0.5 mg.



Figure 27: TG-experiments with Mowiol 56-98 having different initial masses $(HR = 2 \text{ K min}^{-1}, 6 \text{ I h}^{-1} \text{ NTP}).$

5.6.3 Discrimination between thermal decomposition and evaporation during TGexperiments

Both PVOH types and their ionogels were measured under nitrogen and helium atmosphere of 6 l h^{-1} (NTP) and different heating rates. All measured samples show a pure thermal decomposition. Figure 28 exemplarily shows the thermogravimetric measurement of the Mowiol 56-98 under nitrogen and helium atmosphere of 6 l h^{-1} (NTP) and temperature rate 2 K min⁻¹ in crucible made of quartz glass.



Figure 28: TG-experiment of Mowiol 56-98 under nitrogen (N₂) and helium (He) atmosphere (HR = 2 K min⁻¹, 6 I h⁻¹ NTP).

5.6.4 Kinetics of thermal decomposition of Mowiol 56-98 and Mowiol 40-88

The measurements were made under nitrogen atmosphere of 6 l min⁻¹ (NTP) and heating rates of 0.1 K min⁻¹, 0.5 K min⁻¹, 1 K min⁻¹, 2 K min⁻¹ and 10 K min⁻¹ using samples with initial masses of 6 ± 0.5 mg. Figure 29 shows the normalized rate of mass loss (DTG signal) of the Mowiol 56-98 and Mowiol 40-88 in relation to the temperature. The kinetic model was fitted at the first curve of the normalized rate of mass loss curve according to Eq. (4.14).



Figure 29: TG-experiments with Mowiol 56-98 and Mowiol 40-88 and the modelled fit for pure thermal decomposition (Eq. (4.14)) (HR = 2 K min⁻¹, 6 l h⁻¹ NTP).

The result of the kinetic computation of the thermal decomposition of the PVOH types are shown in Table 19.

1410	Wi01 40 00.			
	Pre-exponential	Activation energy	Temperature range	Rate constant
	factor	Ea	of the evaluation	k in s⁻¹
	k₀ in s⁻¹	in kJ mol ⁻¹	in °C	at 220°C
Mowiol 56-98				
and	7.89 10 ¹³	175	150 - 240	2.1 10 ⁻⁵
Mowiol 40-88				

Table 19:The kinetic parameters of the thermal decomposition of the Mowiol 56 - 98 and
Mowiol 40-88.

For typical vinyl polymers the thermal degradation involves breaking of C-C bonds whose bond energy is around 350 kJ mol⁻¹. Although, thermal degradation already occurs above 200-300 °C because of the inherent weak link sites of the polymer chain. Typical weak sites include head-to-head links, hydroperoxy and peroxy structures. Consequently, once the macro radicals are formed, further degradation occurs via various radical pathways whose activation

energies are markedly smaller than the C-C bond energy. For this reason, the effective activation energy varies throughout the process tending to be lower, representing the process of initiation at the weak links [49]. This was proven for thermal decomposition of poly(vinyl alcohol) 98 - 99% hydrolyzed, MW 13 000 - 23 000. At conversion of 15 to 60% interval the decomposition, the activation energy was nearly constant, ranging from 120 - 170 kJ mol⁻¹ [96]. Thus, the calculated activation energies of about 175 kJ mol⁻¹ seems to be reasonable.

In the following the maximum operating temperature is calculated using the kinetic parameters of Table 19.

5.6.5 Maximum operating temperature of Mowiol 56-98 and Mowiol 40-88 with regard to thermal decomposition

The maximum operating temperature was calculated through Eq. (4.15). For an industrial process, losses of 1% per year and for laboratory applications 1% per month (30 days) were determined. The results are shown in Table 20. For comparison the maximum operating temperature of the IL [EMIM][MeSO₃] with regard to thermal decomposition is also shown.

Table 20: Maximum operating temperature, for laboratory applications $T_{max,1\%/m}$ and for
industrial applications $T_{max,1\%/a}$.

Mowiol type	T _{max,1%/m} in °C	T _{max,1%/a} In °C
Mowiol 56-98 and Mowiol 40-88	137	118
[EMIM][MeSO ₃]	181	160

It can be seen that the polymers are less stable than the selected ionic liquid. In the following the IL-polymer-mixtures are also characterized using their TGA data.

5.7 Thermogravimetrical characterization of the IL-polymer mixtures

Using the prepared IL-polymer mixtures / ionogels (see Section 5.2), non-isothermal TGexperiments were conducted at different heating rates under He and N₂ atmosphere. The normalized rate of mass loss curves exhibit a small degradation peak around 240 °C and furthermore a big degradation signal at 260-270 °C. The first step is due to the existence of the PVOH in the mixture and the second curve occurs from the presence of the ionic liquid [EM-IM][MeSO₃]. The two degradation processes (polymer, ionic liquid [EMIM][MeSO₃]) start taking place in almost the same temperature range; so discrimination between them is very difficult. The first small peak can be better recognized at higher concentrations of PVOH in the mixtures. It lies in at the same temperature range as the first peak of the thermal decomposition of the pure PVOH sample. Hence, the PVOH is the limiting component with regard to thermal decomposition of the maximum operating temperature.

The kinetic model using the kinetic parameters of the thermal decomposition of the pure Mowiol 56-98 (shown in Table 19) are used to model the normalized rate of mass loss according to Eq. (4.14) assuming that only the Mowiol 56-98, which means the 9.8 wt% of the initial mass of the IL – polymer mixture is decomposing. Figure 30 shows the modelled curve of the 9.8 wt% Mowiol 56-98 in [EMIM][MeSO₃] mixture. Comparison of predicted and experimental data demonstrates that the first curve is almost entirely caused from the thermal decomposition of the PVOH. Figure 30 also shows the thermal decomposition of the IL – polymer mixtures compared to their pure components.



Figure 30: Normalized rate of mass loss of pure Mowiol 56-98, pure [EMIM][MeSO₃], 4.8 wt% Mowiol 56-98 mixture in [EMIM][MeSO₃], 9.8 wt% Mowiol 56-98 in [EMIM][MeSO₃] mixture and the predicted normalized rate of mass loss assuming a pure thermal decomposition of 9.8 wt% Mowiol during the experiment (HR = 2 K min⁻¹, 6 l h⁻¹ N₂ NTP).
Figure 31 shows the thermal degradation of the 5.2 wt% Mowiol 40-88 in [EMIM][MeSO₃] mixture and the 9.9 wt% Mowiol 40-88 in [EMIM][MeSO₃] mixture compared to their pure components Mowiol 40-88 and [EMIM][MeSO₃] with heating rate of 2 K min⁻¹ under nitrogen atmosphere of 6 I h⁻¹ (NTP). In the same way the normalized rate of mass loss of the 10 wt% Mowiol 40-88 in [EMIM][MeSO₃] is modelled using the kinetics of the thermal decomposition of the pure Mowiol 40-88.



Figure 31: Thermal degradation of pure Mowiol 40-88, pure [EMIM][MeSO₃], 5.2 wt% Mowiol 40-88 ionogel in [EMIM][MeSO₃], 9.9 wt% Mowiol 40-88 ionogel in [EMIM][MeSO₃] and the predicted normalized rate of mass loss assuming a pure thermal decomposition of 9.8 wt% Mowiol during the experiment(HR = 2 K min⁻¹, $6 l h^{-1} N_2$ NTP).

In conclusion, the thermal stability of the poly(vinyl alcohols) determines the thermal stability of the IL - polymer mixtures.

After having characterized the samples used in this work in terms of density, viscosity and thermal stability, their suitability for gas purification should be validated. First the results of the absorption of hydrogen sulfide in the pure ionic liquid [EMIM][MeSO₃] are presented and compared with literature data.

5.8 Henry coefficient of H₂S in [EMIM][MeSO₃]

Table 21 shows the Henry coefficient and activity coefficient for three different temperatures. The Henry coefficient was calculated by the linear fits of Figure 32. The activity coefficient is calculated through Eq. (2.8).



Temperature in °C	Henry Coefficient in mbar	
22	3924	
32	5041	
52	9664	



Figure 32: Partial Pressure of H₂S dependence on molar fraction x_{H2S} in [EMIM][MeSO₃].

The question arises if the ionic liquid [EMIM][MeSO₃] is a good absorbent for hydrogen sulfide compared to the commercial solvents. Figure 33 shows the hydrogen sulfide absorption in different solvents at 20 °C (the absorption in H₂O is at 25 °C and in [EMIM][MeSO₃] at 22 °C). The compared absorbents are water (H₂O) [64], methane [64] and N-methylpyrrolidone [64]. Furthermore it shows the comparison with the H₂S absorption in the ionic liquid 1-(2-hydroxyethyl)-3-methylimidazolium tetrafluoroborate, [hemim][BF₄] [97] at 30 °C. In conclusion, as shown in Figure 33, the ionic liquid $[EMIM][MeSO_3]$ has a better absorption capacity from the compared solvents. For an absorption temperature of 22 °C, the Henry coefficient of the H₂S in the $[EMIM][MeSO_3]$ is by a factor of 1,5 lower compared to the N-methylpyrrolidone at 20 °C. The Henry coefficient of the H₂S in $[EMIM][MeSO_3]$ is for a temperature of 32 °C by a factor of 5,7 lower compared to the ionic liquid $[hemim][BF_4]$.

The [EMIM][MeSO₃] could be an alternative solvent for the absorption of the hydrogen sulfide from its gas not only primilary in the laboratory but also in the industrial-scale application of research.



Figure 33: Experimental data of the hydrogen sulfide absorption compared to solvents from the literature.

After the measurements, the color of the [EMIM][MeSO₃] has gotten darker without showing any kind of decrease in the absorption capacity. Nuclear magnetic resonance spectroscopy (NMR) measurements showed that there was no change in the formation of the IL.

To certify that there is almost no H_2S in the absorption column after the desorption, a defection reaction was used. A beaker was filled with 15 g cupric sulfate $CuSO_4^-$ and 40 ml of water. The mixture was stirred taking a blue color. Then 5 ml IL from the absorption column were taken and added to the mixture. The color almost didn't change.

After that a flow of 8000 ppm H_2S/N_2 gas was passed through the column. At the saturation point, the flow was stopped. A sample of 5 ml IL was taken again and added to a 15 g $CuSO_4^-$ and 40 ml of water mixture. The color got darker and after 3 hours, black particles could be recognized. The difference can be noticed in Figure 34.



Figure 34: a. $CuSO_4^-/H_2O$ mixture with a sample of IL at its saturation point with H_2S , b. $CuSO_4^-/H_2O$ mixture, c. $CuSO_4^-/H_2O$ mixture with a sample of the IL after the last desorption with N_2 flow.

The ionic liquid $[EMIM][MeSO_3]$ has a good absorption and desorption capacity for the H₂S. In the following, the results of the ionogel preparation are presented.

5.9 Dehydration of gas with the ionic liquid [EMIM][MeSO₃]

The validation of the gas dehydration plant was first checked using as an absorbent the pure ionic liquid [EMIM][MeSO₃]. A layer of about 5 g [EMIM][MeSO₃] was filled in the recess of the absorption apparatus. The experiment was accomplished at four different combinations of absorbent and dew point temperatures. After the end of the absorption measurement, a sample was taken from the recess and its water concentration was measured via Karl Fischer Titration (KF Coulometer 756/831, Metrohm). This value was compared to the calculated values from the experimental data of the absorption measurement as shown in Table 22.

Absorbent	Dew	Molar fraction X	Molar fraction X calculated from	Activity
temperature	point	calculated from the	the water concentration of the	Coefficient
in °C	in °C	experimental data	Karl Fischer Titration data	γ
36.8	23.5	0.81	-	0.58
47.1	24	0.67	0.68	0.41
46	17.2	0.63	-	0.31
56	2.4	0.28	0.31	0.16

Table 22: Results of the gas dehydration using as an absorbent a layer of [EMIM][MeSO₃].

The difference between the molar fraction of the last measurement could be caused by the absorbing facility of the ionic liquid. It might have already absorbed a small amount of water while putting it in the absorption apparatus. The results of the molar fraction calculation from the experimental data and the measured one with the Karl Fischer Titration are quite satisfying. This confirms the validation of the absorption process. The results are furthermore compared to literature data [20] in Figure 35.



Figure 35: Experimental data of the water absorption with pure [EMIM][MeSO₃] compared to the literature data [20].

Comparison of the experimental data with those from literature shows that the absorption experiments and the gas dehydration plant works successfully. In the following the ionic liquid - polymer mixtures are used as absorbent with the same experimental conditions as the measurements with the pure [EMIM][MeSO₃].

5.10 Dehydration of gas with the PVOH - [EMIM][MeSO₃] mixtures

At next the absorption process was accomplished using the prepared ionogels. An ionogel layer of about 6 mg was put in the recess of the absorption apparatus. The water content of the ionogel was determined before the measurement and after that via Karl Fischer Titration. From the difference, the absorbed water could be calculated.

The experiment was accomplished with two IL-polymer mixtures as absorbents. The 9.8 wt% Mowiol 56-98 in [EMIM][MeSO₃] ionogel and with the 9.9 wt% Mowiol 40-88 in [EM-IM][MeSO₃] ionogel at an absorbent temperature of 42 °C and three different dew points. The results are furthermore compared to literature data [20] of the pure ionic liquid [EM-IM][MeSO₃] in Figure 36.



Figure 36: Experimental data of the water absorption in PVOH - [EMIM][MeSO₃] mixtures at 42 °C compared to the literature data [20].

The IL – polymer mixtures have successfully absorbed the water having a small deviation from the literature data of the pure ionic liquid. In this way, it can be figured out that the polymer matrix doesn't influence the absorption capacity of the ionic liquid in greater extent.

However, it was noticed that at high water content, the structure of the mixture changes. After the absorption some samples with high molar fractions get white and solid like a gel. Figure 37 exemplary shows the 10 wt% Mowiol 56-98 in [EMIM][MeSO₃] mixture after an absorption process having 0,78 mol% H_2O in [EMIM][MeSO₃].



Figure 37: 10 wt% Mowiol 56-98 in [EMIM][MeSO₃] mixture before the absorption process having 48 mol% H₂O in [EMIM][MeSO₃] (left) and after the absorption process having 78 mol% H₂O in [EMIM][MeSO₃] (right).

It is assumed that the water connects with the polymer matrix because of the small concentration of the ionic liquid. The sample was put in the oven at 110 °C for an hour taking again its initial form.

6 Summary and Outlook

Background and objectives of this work

The interest in ionic liquids (melting point below 100°C; IL) and their potential applications are still rising in academia as well as industry due to the variety of their chemical and physical properties. In separation processes, evaporation losses and product contaminations can be avoided because of their very low vapor pressure. A number of ionic liquids have hygroscopic character, so they can absorb a certain extent of water. This property can be an advantage for gas and fluid drying.

Gas drying is an important separation process for drying of natural gas in order to avoid corrosion and hydrate formation in the pipelines. In the industry, the absorptive gas scrubbing with glycols (especially with triethylene glycol; TEG) as absorbent is well established. However, TEG has two major disadvantages:

- TEG has a relatively high vapor pressure and
- TEG is not stable against oxidative attack. Hence, the regeneration of water loaded TEG with air stripping gas is not feasible due to the oxidative decomposition of TEG (formation of organic acids, corrosion problems)

The absorption of hydrogen sulfide is also of great importance in the gas industry. The toxicity and corrosive properties of H_2S dictate stringent control of its release into the environment and contact of aqueous solutions of H_2S with iron and steel as tanks, piping, valves and pumps. The most common way for the removal of acidic components from gas streams are amine solutions.

In contrast to various studies on the absorption of CO_2 and SO_2 in ILs, the number of publications on absorption of water as well as hydrogen sulfide is still low. ILs could be alternative absorbents for water and hydrogen sulfide absorption too.

At the beginning of the 21. Century, ionic liquids were immobilized on porous supports in order to combine e.g. the advantages of both the homogenous and heterogeneous catalysis. Other researchers tried to combine both the unique properties of polymers and ILs. This leads to supported membranes and the so-called "ionogels". Ionic liquids confined in gel matrices make them suitable in various applications e.g. stable electrolytes in dye-sensitized solar cells, secondary batteries, electrochromic displays, electrolytic membranes and perhaps even for gas separation processes.

The objective of the present work is on the one hand the immobilization of the ionic liquids in a polymer matrix and the evaluation, if these hybrid materials are suitable for gas dehydration. On

the other hand, absorption of H_2S in the neat ionic liquid [EMIM][MeSO₃], which is a common impurity besides water vapor in natural gas, is in the main focus.

Key results

The hygroscopic ionic liquid [EMIM][MeSO₃] was immobilized into the three polymers, the agar agar and two types of poly(vinyl alcohol) (PVOH). The high amount of water in the agar agar-[EMIM][MeSO₃] ionogels was the reason why the PVOH-[EMIM][MeSO₃] ionogels were chosen for the gas dehydration. First the main components of the ionic liquid – polymer mixtures were characterized. The thermal decomposition of the [EMIM][MeSO₃] was calculated with a "model free" method, the isoconversional method and compared with literature data. The calculation of the kinetics of thermal decomposition using the isoconversional method took considerable time without having any advantage compared to the TGA method established at the Chair of Chemical Engineering of University of Bayreuth. At next the thermal decomposition of the two types of PVOH (Mowiol 56-98, Mowiol 40-88) was also determined with the TGA method. Furthermore the density and viscosity of the prepared IL – polymer mixtures were measured. IL - polymer mixtures with about 10wt% PVOH in [EMIM][MeSO₃] were used for the gas dehydration measurements. The results compared with the literature data for the absorption of water in neat [EMIM][MeSO₃], were satisfactorily. This means that the polymer matrix doesn't influence the absorption capacity of the ionic liquid.

The absorption of the hydrogen sulfide was accomplished using the $[EMIM][MeSO_3]$ as a solvent. The measurements showed that the ionic liquid $[EMIM][MeSO_3]$ is suitable for the purification of gas from its hydrogen sulfide component. For the absorption temperature of 22 °C, the activity coefficient of H₂S in the $[EMIM][MeSO_3]$ is by a factor of about 1.5 lower compared to the Nmethylpyrrolidone at 20°C. The activity coefficient of the H₂S in $[EMIM][MeSO_3]$ is for a temperature of 32 °C by a factor of 5,7 lower compared to the ionic liquid $[hemim][BF_4]$.

Conclusion and Outlook

In the present work, it shows that the ionic liquid $[EMIM][MeSO_3]$ can be immobilized into the polymer poly(vinyl alcohol) without losing its absorption capacity. These hybrid materials have to be stored carefully in order to maintain the initial water content. The pure ionic liquid could be dried using a rotary evaporator while for the ionogels it is not easy because of its colloidal composition. A solution could be the preparation of the ionogels under vacuum und their storage into tight closed glasses. On the basis of the results, the main idea to get a kind of "fixed bed absorber" seems to be possible since the IL - polymer mixtures keep the absorption capacity of the ionic liquid. Further studies concerning the ternary mixtures $H_2O - IL - polymer$ should be conducted in

order to get more information about the mechanism of gelation, rheological behavior, miscibility gaps and informations about the mass transfer in such a gel layer.

The investigation on separating the hydrogen sulfide (H_2S) with the ionic liquid [EMIM][MeSO₃] from a gas stream showed that the [EMIM][MeSO₃] has a good absorption capacity. It is already proven that the [EMIM][MeSO₃] is an alternative drying agent to the absorbent TEG commonly used for industrial gas drying. In the ideal case, both gases would be absorbed simultaneously. Therefor it should be furthermore investigated if the [EMIM][MeSO₃] can also separate H_2S from natural gas in presence of water vapor.

7 References

- [1] A.L. Kohl, R. Nielsen, *Gas purification*, 5th ed., Gulf Pub., Houston, Tex. **1997**.
- [2] E.G. Hammerschmidt, Formation of Gas Hydrates in Natural Gas Transmission Lines, Ind. Eng. Chem. **1934** 26 (8), 851. DOI: 10.1021/ie50296a010.
- [3] S. Ueberhorst, *Energieträger Erdgas: Exploration, Produktion, Versorgung,* 3rd ed., Die Bibliothek der Technik, Bd. 194, Verl. Moderne Industrie, Landsberg/Lech **1999**.
- [4] Verfahren der Fasaufbereitung (Erdgas-Brenngas-Synthesegas) (Ed: Schmidt).
- [5] S.O. Derawi, M.L. Michelsen, G.M. Kontogeorgis, E.H. Stenby, Application of the CPA equation of state to glycol/hydrocarbons liquid–liquid equilibria, Fluid Phase Equilibria 2003 209 (2), 163. DOI: 10.1016/S0378-3812(03)00056-6.
- [6] W.G. Lloyd, Inhibition of Polyglycol Autoxidation, J. Chem. Eng. Data 1961 6 (4), 541. DOI: 10.1021/je60011a019.
- P.W. Brown, W.J. Rossiter, K.G. Galuk, A mass spectrometric investigation of the thermal oxidative reactivity of ethylene glycol, Solar Energy Materials 1986 13 (3), 197. DOI: 10.101 6/0165-1633(86)90018-3.
- [8] O. Zech, M. Kellermeier, S. Thomaier, E. Maurer, R. Klein, C. Schreiner, W. Kunz, Alkali metal oligoether carboxylates--a new class of ionic liquids, Chemistry (Weinheim an der Bergstrasse, Germany) 2009 15 (6), 1341. DOI: 10.1002/chem.200801806.
- [9] M. Freemantle, An Introduction to ionic liquids, RSC Pub., Cambridge, UK 2010.
- [10] T. Welton, Room-Temperature Ionic Liquids. Solvents for Synthesis and Catalysis, Chem. Rev. 1999 99 (8), 2071. DOI: 10.1021/cr980032t.
- [11] R.D. Rogers, K.R. Seddon, Chemistry. Ionic liquids--solvents of the future?, Science (New York, N.Y.) 2003 302 (5646), 792. DOI: 10.1126/science.1090313.
- [12] J.F. Brennecke, E.J. Maginn, *Ionic liquids: Innovative fluids for chemical processing, AIChE J.* **2001** 47 (11), 2384. DOI: 10.1002/aic.690471102.
- [13] J. Latz, Entschwefelung von Mitteldestillaten f
 ür die Anwendung in mobilen Brennstoffzellen-Systemen, Schriften des Forschungszentrums J
 ülich / Reihe Energie & Umwelt, Bd. 14, Forschungszentrum, Zentralbibliothek, J
 ülich 2008.
- [14] A. Vioux, L. Viau, S. Volland, J. Le Bideau, Use of ionic liquids in sol-gel; ionogels and applications, Comptes Rendus Chimie 2010 13 (1-2), 242. DOI: 10.1016/j.crci.2009.07.002.
- [15] P. Wasserscheid, T. Welton, *Ionic liquids in synthesis*, 2nd ed., Wiley-VCH, Weinheim **2008**.
- P. Wasserscheid, W. Keim, Ionic Liquids—New "Solutions" for Transition Metal Catalysis, Angew. Chem. Int. Ed. 2000 39 (21), 3772. DOI: 10.1002/1521-3773(20001103)39:21<3772: AID-ANIE3772>3.0.CO;2-5.
- [17] Perez De Los Rios, Antonia, Hernandez Fernandez, Francisco Jose, *Ionic liquids in separation technology*.
- [18] X. Han, D.W. Armstrong, Ionic liquids in separations, Accounts of chemical research 2007 40 (11), 1079. DOI: 10.1021/ar700044y.

- [19] Handbook of Green Chemistry Green Solvents: Volume 4 Supercritical Solvents (Eds: P.T. Anastas, W. Leitner, P.G. Jessop), 1st ed., Wiley-VCH, Weinheim 2014.
- [20] Krannich Michel, Charakterisierung binärer Mischungen aus Wasser und reinen ionischen Fluiden und deren Anwendungen zur Gastrocknung durch Absorption, Doktorarbeit, Lehrstuhl für Chemische Verfahrenstechnik Universität Bayreuth **2015**.
- [21] J. Le Bideau, L. Viau, A. Vioux, *Ionogels, ionic liquid based hybrid materials, Chemical Society reviews* **2011** *40* (*2*), 907. DOI: 10.1039/c0cs00059k.
- [22] D. Mecerreyes, Applications of Ionic Liquids in Polymer Science and Technology, Springer Berlin Heidelberg, Berlin, Heidelberg 2015.
- [23] S.J. Craythorne, K. Anderson, F. Lorenzini, C. McCausland, E.F. Smith, P. Licence, A.C. Marr, P.C. Marr, The co-entrapment of a homogeneous catalyst and an ionic liquid by a sol-gel method: recyclable ionogel hydrogenation catalysts, Chemistry (Weinheim an der Bergstrasse, Germany) 2009 15 (29), 7094. DOI: 10.1002/chem.200801809.
- [24] A. Zamboulis, N. Moitra, Moreau, Joël J. E., X. Cattoën, Wong Chi Man, Michel, Hybrid materials: versatile matrices for supporting homogeneous catalysts, J. Mater. Chem. 2010 20 (42), 9322. DOI: 10.1039/C000334D.
- [25] T.J. Trivedi, D.N. Srivastava, R.D. Rogers, A. Kumar, Agarose processing in protic and mixed protic–aprotic ionic liquids: dissolution, regeneration and high conductivity, high strength ionogels, Green Chem. 2012 14 (10), 2831. DOI: 10.1039/c2gc35906e.
- [26] H.D. Bean, Georgia Institute of Technology, Prebiotic Synthesis of Nucleic Acids, Georgia Institute of Technology 2008.
- [27] N. Merkel, C. Weber, M. Faust, K. Schaber, Influence of anion and cation on the vapor pressure of binary mixtures of water+ionic liquid and on the thermal stability of the ionic liquid, Fluid Phase Equilibria 2015 394, 29. DOI: 10.1016/j.fluid.2015.03.001.
- [28] H. Olivier-Bourbigou, L. Magna, D. Morvan, Ionic liquids and catalysis: Recent progress from knowledge to applications, Applied Catalysis A: General 2010 373 (1-2), 1. DOI: 10.1016/j.apcata.2009.10.008.
- [29] Y.U. Paulechka, G.J. Kabo, A.V. Blokhin, O.A. Vydrov, J.W. Magee, M. Frenkel, Thermodynamic Properties of 1-Butyl-3-methylimidazolium Hexafluorophosphate in the Ideal Gas State †, J. Chem. Eng. Data 2003 48 (3), 457. DOI: 10.1021/je025591i.
- [30] R. Chang, *Physical chemistry for the biosciences*, University Science, Sansalito, Calif. 2005.
- [31] F. Heym, J. Haber, W. Korth, Etzold, B. J. M., A. Jess, Vapor Pressure of Water in Mixtures with Hydrophilic Ionic Liquids - A Contribution to the Design of Processes for Drying of Gases by Absorption in Ionic Liquids, Chem. Eng. Technol. 2010 33 (10), 1625. DOI: 10.1002/ceat.201000146.
- [32] F. Heym, W. Korth, B. Etzold, C. Kern, A. Jess, Determination of vapor pressure and thermal decomposition using thermogravimetrical analysis, Thermochimica Acta 2015. DOI: 10.1016/j.tca.2015.03.020.

- [33] Florian Heym, Dampfdruck und thermische Zersetzung reiner und geträgerter ionischer Flüssigkeiten, BoD – Books on Demand, 2014.
- [34] B. Hasse, J. Lehmann, D. Assenbaum, P. Wasserscheid, A. Leipertz, A.P. Fröba, Viscosity, Interfacial Tension, Density, and Refractive Index of Ionic Liquids [EMIM][MeSO 3], [EM-IM][MeOHPO 2], [EMIM][OcSO 4], and [BBIM][NTf 2] in Dependence on Temperature at Atmospheric Pressure †, J. Chem. Eng. Data 2009 54 (9), 2576. DOI: 10.1021/je900134z.
- [35] Sigma-Aldrich, 1-Ethyl-3-methylimidazolium methanesulfonate, Sicherheitsblatt Version
 5.0, http://www.sigmaaldrich.com/catalog/product/aldrich/29164?lang=de®ion=DE, accessed 8 April 2015.
- [36] F. Heym, W. Korth, Etzold, B. J. M., G. Michos, A. Jess, Gastrocknung durch Absorption in ionischen Flüssigkeiten, Chemie Ingenieur Technik 2010 82 (9), 1581. DOI: 10.1002/cite.20105 0355.
- [37] Belle Lowe, *Experimental Cookery From The Chemical And Physical Standpoint*, John Wiley & Sons **1937**.
- [38] K. MacKinnon, *The Ecology of Kalimantan*, Periplus Editions **1996**.
- [39] D.J. McHugh, Production and utilization of products from commercial seaweeds, FAO fisheries technical paper, Vol.288, Food and Agriculture Organization of the United Nations, Rome 1987.
- [40] Jones, W. G. M., S. Peat, 42. The constitution of agar, J. Chem. Soc. 1942, 225. DOI: 10.1039/jr9420000225.
- [41] T. Singh, T.J. Trivedi, A. Kumar, *Dissolution, regeneration and ion-gel formation of agarose in room-temperature ionic liquids, Green Chem.* **2010** *12 (6),* 1029. DOI: 10.1039/b927589d.
- [42] A. Nussinovitch, *Hydrocolloid applications: Gum technology in the food and other industries,* 1st ed., Blackie Academic & Professional, London, New York **1997**.
- [43] R.L. Whistler, J.N. BeMiller, *Industrial gums, polysaccharides and their derivatives,* 2nd ed., Academic Press, New York **1973**.
- [44] Carl Roth, Agar agar Kobe I, www.carlroth.com, accessed 15 April 2015.
- [45] D.J. McHugh, FAO fisheries technical paper, Vol.288, Food and Agriculture Organization of the United Nations, Rome 1987.
- [46] Kuraray Europe GmbH, http://www.kuraray.eu, accessed 23 June 2015.
- [47] I. Sakurada, *Polyvinyl alcohol fibers*, International fiber science and technology series, v. 6, M. Dekker, New York **1985**.
- [48] Clariant, Mowiol Polyvinyl Alcohol, http://www2.cbm.uam.es/confocal/Manuales/mowiol. pdf, accessed 6 March 2015.
- [49] S. Vyazovkin, N. Sbirrazzuoli, Isoconversional Kinetic Analysis of Thermally Stimulated Processes in Polymers, Macromol. Rapid Commun. 2006 27 (18), 1515. DOI: 10.1002/marc.200 600404.
- [50] S. Slomkowski, J.V. Alemán, R.G. Gilbert, M. Hess, K. Horie, R.G. Jones, P. Kubisa, I. Meisel,
 W. Mormann, S. Penczek, Stepto, Robert F. T., *Terminology of polymers and polymerization*

processes in dispersed systems (IUPAC Recommendations 2011), Pure and Applied Chemistry **2011** 83 (12). DOI: 10.1351/PAC-REC-10-06-03.

- [51] M. Nič, J. Jirát, B. Košata, A. Jenkins, A. McNaught, *IUPAC Compendium of Chemical Termi*nology, IUPAC, Research Triagle Park, NC **2009**.
- [52] Katsuyoshi Nishinari, Some Thoughts on The Definition of a Gel Springer, http://link. springer.com/chapter/10.1007/978-3-642-00865-8_12, accessed 27 April 2015.
- [53] Almdal, K., et al., *Towards a phenomenological definition of the term 'gel'*. Polymer Gels and Networks 1.1 (1993): 5-17.
- [54] Y. Osada, A.R. Khokhlov, *Polymer gels and networks*, Marcel Dekker, New York **2002**.
- [55] K. Nishinari, in *Gels: Structures, Properties, and Functions*, Springer Berlin Heidelberg, Berlin, Heidelberg **2009**.
- [56] *Handbook of Hydrocolloids* (Eds: G.O. Phillips, P.A. Williams), 2nd ed., Woodhead Publishing Series in Food Science, Technology and Nutrition, Woodhead Pub, Cambridge **2009**.
- [57] Danilo DeRossi, Kanji Kajiwara, Yoshihito Isada, Aizo Yamauchi, *Polymer Gels: Fundamentals and Biomedical Applications*, Springer Verlag **2012**.
- [58] A.H. Bilge, O. Pekcan, A mathematical characterization of the gel point in sol-gel transition, J. Phys.: Conf. Ser. 2015 574, 012005. DOI: 10.1088/1742-6596/574/1/012005.
- [59] J.E. Martin, D. Adolf, J.P. Wilcoxon, Viscoelasticity of Near-Critical Gels, Phys. Rev. Lett. 1988 61 (22), 2620. DOI: 10.1103/PhysRevLett.61.2620.
- [60] R.G. Larson, *The structure and rheology of complex fluids,* Topics in chemical engineering, Oxford University Press, New York **1999**.
- [61] T.J. Trivedi, K.S. Rao, A. Kumar, Facile preparation of agarose–chitosan hybrid materials and nanocomposite ionogels using an ionic liquid via dissolution, regeneration and sol–gel transition, Green Chem 2014 16 (1), 320. DOI: 10.1039/C3GC41317A.
- [62] Y. Suzaki, T. Taira, K. Osakada, Physical gels based on supramolecular gelators, including host-guest complexes and pseudorotaxanes, J. Mater. Chem. 2011 21 (4), 930. DOI: 10.1039/c0jm02219e.
- [63] C. Yuan, J. Guo, F. Yan, Shape memory poly(ionic liquid) gels controlled by host-guest interaction with β-cyclodextrin, Polymer 2014 55 (16), 3431. DOI: 10.1016/j.polymer.2014.03.
 024.
- [64] A. Jess, P. Wasserscheid, *Chemical technology: An integrated textbook*, Wiley-VCH, Weinheim **2013**.
- [65] J.I. Huertas, N. Giraldo, S. Izquierdo, in *Mass Transfer in Chemical Engineering Processes* (Ed: J. Marko), InTech **2011**.
- [66] Y.A. Çengel, M.A. Boles, *Thermodynamics: An engineering approach*.
- [67] K.L. Sublette, N.D. Sylvester, Oxidation of hydrogen sulfide by Thiobacillus denitrificans: desulfurization of natural gas, Biotechnology and bioengineering 1987 29 (2), 249. DOI: 10.1002/bit.260290216.

- [68] F.W. Sperr, Absorption of Hydrogen Sulfide, Ind. Eng. Chem. 1924 16 (12), 1237. DOI: 10.1021/ie50180a010.
- [69] H.D. Frazier, A.L. Kohl, Selective Absorption of Hydrogen Sulfide from Gas Streams, Ind. Eng. Chem. 1950 42 (11), 2288. DOI: 10.1021/ie50491a032.
- [70] R.R. Bottoms, Organic Bases for Gas Purification, Ind. Eng. Chem. 1931 23 (5), 501. DOI: 10.1021/ie50257a007.
- [71] J.D. Lawson, A.W. Garst, Gas sweetening data: equilibrium solubility of hydrogen sulfide and carbon dioxide in aqueous monoethanolamine and aqueous diethanolamine solutions, J. Chem. Eng. Data 1976 21 (1), 20. DOI: 10.1021/je60068a010.
- [72] G. Astarita, F. Gioia, Hydrogen sulphide chemical absorption, Chemical Engineering Science 1964 19 (12), 963. DOI: 10.1016/0009-2509(64)85103-4.
- [73] Processing Natural Gas, naturalgas.org, accessed 15 April 2015.
- [74] http://www.taluft.com/taluft20020730.pdf, accessed 26 May 2015.
- [75] E.W. McAllister, *Pipeline rules of thumb handbook: Quick and accurate solutions to your everyday pipeline problems,* 7th ed., Gulf Professional/Elsevier, Amsterdam, Boston **2009**.
- [76] H.D. Baehr, *Thermodynamik: Eine Einführung in die Grundlagen und ihre technischen Anwendungen,* 5th ed., Springer Verlag, Berlin, New York **1984**.
- [77] GE Oil & Gas, Inlet Air Cooling **2008**, http://site.ge-energy.com/businesses/ge_oilandgas/en /literature/en/downloads/inletair_cooling.pdf, accessed 28 July 2015.
- [78] R. Chang, *Physical chemistry for the chemical and biological sciences*, University Science Books, Sausalito, Calif. **2000**.
- [79] C. Lüdecke, D. Lüdecke, *Thermodynamik*, Springer Berlin Heidelberg, Berlin, Heidelberg **2000**.
- [80] D.R. Stull, Vapor Pressure of Pure Substances. Organic and Inorganic Compounds, Ind. Eng. Chem. 1947 39 (4), 517. DOI: 10.1021/ie50448a022.
- [81] K.R. Hall, Numerical data and functional relationships in science and technology, Springer, Berlin [u.a.] **2000**.
- [82] T. Foken, Angewandte Meteorologie: Mikrometeorologische Methoden, 2nd ed., Springer-Verlag Berlin Heidelberg, Berlin, Heidelberg **2006**.
- [83] New York Glycerine Producers' Association, *Physical properties of glycerine and its solutions.* **1963**.
- [84] http://www.uni-magdeburg.de/isut/LSS/Lehre/Arbeitsheft/IV.pdf, accessed 23 July 2015.
- [85] Wasser und seine Eigenschaften, http://www.wissenschaft-technik-ethik.de/wasser __dichte.html, accessed 23 July 2015.
- [86] http://msdssearch.dow.com/PublishedLiteratureDOWCOM/dh_0032/0901b803800322 82.pdf?filepath=glycerine/pdfs/noreg/115-00656.pdf&fromPage=GetDoc, accessed 23 June 2015.
- [87] C. Schießl, "Thermische Analyse Möglichkeiten zur Untersuchung von dentalen Kunststoffen". Diss. Regensburg: Universität Regensburg, 2009.

- [88] T. Ozawa, Kinetic analysis of derivative curves in thermal analysis, Journal of Thermal Analysis 1970 2 (3), 301. DOI: 10.1007/BF01911411.
- [89] S. Vyazovkin, A.K. Burnham, J.M. Criado, L.A. Pérez-Maqueda, C. Popescu, N. Sbirrazzuoli, ICTAC Kinetics Committee recommendations for performing kinetic computations on thermal analysis data, Thermochimica Acta 2011 520 (1–2), 1. DOI: 10.1016/j.tca.2011.03.034.
- [90] W. Hemminger, Methoden der thermischen Analyse. Anleitungen für die chemische Laboratoriumspraxis. Berlin und Heidelberg: Springer, 1989.
- [91] J. Málek, The kinetic analysis of non-isothermal data, Thermochimica Acta 1992 200 (0), 257. DOI: 10.1016/0040-6031(92)85118-F.
- [92] M.J. Starink, The determination of activation energy from linear heating rate experiments: a comparison of the accuracy of isoconversion methods, Thermochimica Acta 2003 404 (1–2), 163. DOI: 10.1016/S0040-6031(03)00144-8.
- [93] S. Vyazovkin, K. Chrissafis, Di Lorenzo, Maria Laura, N. Koga, M. Pijolat, B. Roduit, N. Sbirrazzuoli, J.J. Suñol, ICTAC Kinetics Committee recommendations for collecting experimental thermal analysis data for kinetic computations, Thermochimica Acta 2014 590 (0), 1. DOI: 10.1016/j.tca.2014.05.036.
- [94] H.L. Friedman, Kinetics of thermal degradation of char-forming plastics from thermogravimetry. Application to a phenolic plastic, J. polym. sci., C Polym. symp. 1964 6 (1), 183. DOI: 10.1002/polc.5070060121.
- [95] David Sonnleitner, Aufbau und Validierung einer diskontinuierlichen Gastrocknungsanlage zur Bestimmung der Aktivitätskoeffizienten hochviskosen IL - polymer Mischungen, Studienarbeit, Universität Bayreuth 2015.
- [96] D.M. Fernandes, A.W. Hechenleitner, E.G. Pineda, Kinetic study of the thermal decomposition of poly(vinyl alcohol)/kraft lignin derivative blends, Thermochimica Acta 2006 441 (1), 101. DOI: 10.1016/j.tca.2005.11.006.
- [97] M. Shokouhi, M. Adibi, A.H. Jalili, M. Hosseini-Jenab, A. Mehdizadeh, Solubility and Diffusion of H 2 S and CO 2 in the Ionic Liquid 1-(2-Hydroxyethyl)-3-methylimidazolium Tetra-fluoroborate, J. Chem. Eng. Data 2010 55 (4), 1663. DOI: 10.1021/je900716q.