influence of the size of the counter ion on the electrical characteristics and the EL emission spectra was found.

Experimental

The dielectric properties of the films have been determined using a Solatron-Schlumberger SI-1260 in the frequency interval from 10^{-1} to 10^6Hz. Dielectric spectra were measured both for untreated films and after annealing at approx. 100 °C. Absorption spectra were recorded with a Perkin-Elmer Lambda-9 spectrophotometer. Photoluminescence spectra were recorded using a commercially available spectrofluorometer (Spex Fluorolog 212) with single photon-counting detection (Hamamatsu R928P photomultiplier) and a 450 W Xenon lamp as excitation source. PL spectra were detected normal to the sample surface. The angle of incidence of the excitation light was 22.5° from the sample surface normal in order to minimize re-absorption. Samples of the light-emitting devices were prepared by spin coating the polymer solution onto ITO-covered glass substrates. The upper 50–55 nm thick aluminum electrode was prepared by vacuum evaporation. Film thicknesses were measured using a Tencor alpha-step 200 profilometer. Current–voltage characteristics were recorded with a Keithley 236 source measure unit. Electroluminescence spectra were measured using a triple-grating spectrograph EG&G Model 1235 with a 1200 line/mm grating and single photon-counting detection (Hamamatsu R928P photomultiplier). The total light output was determined with a calibrated silicon photodiode Newport Model 818 UV in connection with an optical power meter (Newport Model 835). The measured EL and PL emission spectra were corrected for the spectral response of the detection systems, as determined with a calibrated halogen lamp (CL2 Bentham 18175).

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[1] a) G. Grem., G. Leditzky, B. Ullrich,. G. Leising, *Adv. Mater.* **1992**, *4*, 36.
   b) G. Grem, G. Leising *Synth. Met.* **1993**, *55-57*, 4105.
   c) Y. Yang, Q. Pei, A. J. Heeger, *J. Appl. Phys.* **1996**, *79*, 934.
[2] a) J. Grüner, P. J. Hamer, R. H. Friend, H.-J. Huber, U. Scherf, A. B. Holmes, *Adv. Mater.* **1994**, *6*, 748. b) U. Scherf, K. Müllen, *Makromol. Chem., Rapid Commun.* **1991**, *12*, 489. c) J. Huber, K. Müllen, J. Salbeck, H. Schenk, U. Scherf, T. Stehlin, R. Stern, *Acta Polym.* **1994**, *45*, 244.
[3] V. Cimrová, M. Remmers, D. Neher, G. Wegner, *Adv. Mater.* **1996**, *8*, 146.
[4] D. D. Gebler, Y. Z. Wang, J. W. Blatchford, S. W. Jessen, L.-B. Lin, T. L.Gustafson, H. L.Wang, T. M. Swager, A. G. MacDiarmid, A. J. Epstein, *J. Appl. Phys.* **1995**, *78*, 4264.
[5] P. Heseman, H. Vestweber, J. Pommerehne, R. F. Mahrt, A. Greiner, *Adv. Mater.* **1995**, *7*, 388.
[6] C. Zhang, H. von Seggern, B. Kraabel, H.-W. Schmidt, A. J. Heeger, *Synth. Met.* **1995**, *72*, 185.
[7] M. A. Keegstra, V. Cimrová, D. Neher, U. Scherf, *Macromol. Chem. Phys.*, in press.
[8] H.-J. Brouwer, V. V. Krasnikov, A. Hilberer, J. Wildeman, G. Hadziioannou *Appl. Phys. Lett.* **1995**, *66*, 3404.
[9] G. Wegner, D. Neher, M. Remmers, V. Cimrová, M. Schulze, *Proc. MRS Mtg.*, Boston November **1995**.
[10] I. D. Parker, Q. Pei, M. Marrocco, *Appl. Phys. Lett.* **1994**, *65*, 1272.
[11] I. D. Parker, *J. Appl. Phys.* **1994**, *75*, 1656.
[12] Q. Pei, G. Yu, C. Zhang, Y. Yang, A. J. Heeger, *Science* **1995**, *269*, 1086.
[13] W. Schmidt, *Ph.D. Thesis*, University of Mainz **1996**.
[14] R. Ruikens, G. Wegner, V. Enkelmann, M. Schulze, *Berichte der Bunsenges.*, in press.
[15] U. Lemmer, S. Heun, R. F. Mahrt, U. Scherf, M. Hopmeier, U. Siegener, E. O. Göbel, K. Müllen, H. Bässler, *Chem. Phys. Lett.* **1995**, *240*, 373.
[16] T. Pauck, R. Hennig, M. Perner, U. Lemmer, U. Siegener, R. F. Mahrt, U. Scherf, K. Müllen, H. Bässler, E. O. Göbel, *Chem. Phys. Lett.* **1995**, *244*, 171.

Amorphous Silica Molecular Sieving Membranes by Sol-Gel Processing**

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There has been continued interest in developing microporous ceramic membranes, which have potential applications in the chemical, environmental, energy conversion, and automotive industries because of their many unique characteristics such as good chemical, thermal, and mechanical stability. Several techniques have been used to synthesize porous ceramic membranes, such as sol-gel synthesis,[1–6] phase separation and leaching,[7,8] and chemical vapor deposition.[9–12] Among these, sol-gel processing is the most widely used technique since it can be used to coat tubular and high surface area monolithic supports and potentially allows precise control of the pore structure. Brinker et al.[13,14] have proposed several strategies for synthesis of microporous membranes. De Lange et al.[15,16] have reported experiments in which they have successfully synthesized microporous silica membranes that demonstrate molecular sieving properties. In general, however, a reduction of pore size in microporous ceramic membranes is achieved at the expense of porosity or pore volume and, thus, good separation properties are coupled with a low gas flux. It has remained a great challenge to the research community to synthesize ceramic membranes having micropores with a uniform or very narrow pore size distribution and with a large pore volume.

In the present study, we have investigated general routes to the synthesis of microporous ceramics and ceramic membranes with pores in the ultra-microporous regime (pore radius ≤ 0.5 nm) and with a narrow pore size distribution using an organic template approach by sol-gel processing. The technical approach is conceptually straightforward: to synthesize a dense inorganic–organic hybrid material (without adventitious pores) using the sol-gel method and then to create pores by removing the organic templates from the dense material during pyrolysis at elevated temperatures.[13,17] Our hypotheses in this approach are that the size and shape of pores developed in the membrane are determined by the size and shape of the organic ligands (templates) and that the porosity (i.e., total

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pore volume) is determined by the molar ratio of the inorganic precursor to the organic template-substituted precursor.

In the experiments carried out for this study, the chemical precursors used were tetraethyl orthosilicate, $Si(OC_2H_5)_4$ (TEOS, from Kodak, Rochester, NY), and 3-methacryloxy-propyl trimethoxysilane, $H_2C=C(CH_3)CO_2(CH_2)_3Si(OCH_3)_3$ (MPS, from PCR, Gainesville, FL). Each MPS molecule contains one non-hydrolyzable organic ligand, $H_2C=C(CH_3)CO_2(CH_2)_3$, hereafter also referred to as the organic template. Sols were prepared by mixing TEOS, MPS, C_2H_5OH, H_2O, and HCl in a molar ratio of $1.0:0.25:4.7:6.3:5.3 \times 10^{-3}$ at 60 °C for 90 min under stirring, and aged in a closed bottle for 140 h at 50 °C. The sols diluted with ethanol in a volume ratio of 1:2 were cast as thin sheets in a petri dish and dried rapidly to obtain xerogels or were dip-coated onto porous alumina tubular substrates to form supported films, also referred to as membranes. The alumina support tubes (Membralox from US filter, Warrendale, PA) were asymmetric in structure with an inner layer of mesoporous γ-alumina having an average pore diameter of 5 nm deposited on a α-alumina macroporous tubular substrate. The apparatus and procedure for dip-coating have been described in detail previously.[18,19] Both xerogels and membranes were dried by heating them to 150 °C at 1 °C/min and keeping them at 150 °C for 3 h. The pyrolysis step designed to remove the organic templates consisted of further heating the materials after drying to 350 °C (1 °C/min) in air and holding them at 350 °C for 3 h. This thermal treatment resulted in the formation of white microporous films and xerogels.

The xerogel powders were characterized by means of thermal gravimetric analysis (TGA), differential thermal analysis (DTA, using STA 1500 from Rheometrics, Piscataway, NJ), and nitrogen sorption porosimetry at 77 K (Micromeritics ASAP 2000M, Norcross, GA). Single gas permeation measurements were performed in a home-made apparatus[18,19] on membranes dried at 150 °C and after pyrolysis of the organic templates at 350 °C. For comparison, gas permeation measurements were also performed on the bare porous alumina support tubes. Prior to the gas permeation measurements, all samples were out-gassed at 150 °C in helium for more than 8 h. Four gases—He (purity 99.999 %), N_2 (99.995 %), C_3H_6 (99.5 %), and SF_6 (99.5 %) with kinetic diameters ranging from 0.265 to 0.55 nm (see Table 1)—were chosen for the measurements. Details of the

single gas permeation apparatus and experimental procedures have been described previously.[18,19]

The hybrid inorganic–organic xerogels prepared as described above and dried at 150 °C for 3 h in air exhibited no detectable nitrogen adsorption at 77 K and, thus, are considered to be dense or to contain sufficiently small pores that nitrogen sorption at 77 K is severely kinetically limited.[20] The exact mechanism of formation of these dense hybrid organic–inorganic materials is not yet clear and is currently under investigation. Under comparable polymerization conditions, xerogels formed only from TEOS can exhibit considerable nitrogen adsorption (i.e., are not dense).[2] A possible mechanism for the formation of the dense hybrid materials is that the introduction of MPS into the silica network results in the formation of weakly branched structures due to the presence of a non-hydrolyzable organic ligand on each MPS molecule. In addition, only a short aging time (140 h, about 0.1 gelation time) was applied in this study to limit growth of silicate oligomers and/or polymers. Thus the silicate network formed upon drying would have a very low modulus, which in turn would promote collapse of the network. The effects of a short aging time and the presence of organic templates, therefore, combine to make the possibility of restructuring and/or collapse of the silicate network high, and a relatively dense hybrid organic–inorganic material with respect to nitrogen adsorption porosimetry can be more readily obtained, as compared to xerogels obtained from TEOS alone, or other inorganic polymer precursors.[2]

Figure 1 shows the weight loss and heat evolution of a xerogel during TGA/DTA in air (with a heating rate of 1 °C/min). Two peaks were observed at approximately 180 °C
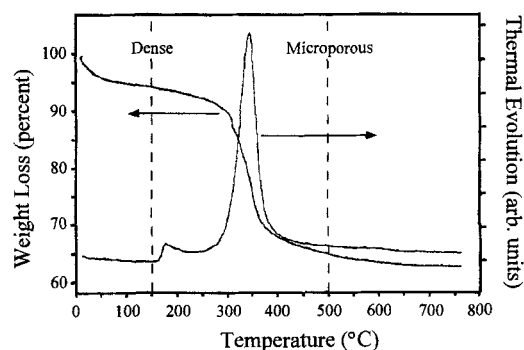

Figure 1. Weight loss and heat evolution of hybrid organic–inorganic xerogel during thermal gravimetric analysis (TGA) and differential thermal analysis (DTA) in air (1 atm). The xerogel was prepared by co-polymerization of MPS and TEOS in a ratio of 1:4. The heating rate was 1 °C/min. The dashed lines indicate the two pyrolysis temperatures used to prepare materials for nitrogen adsorption and gas permeation measurements.

Table 1. Gas permeance and ideal separation factors of various gases through microporous silica membranes ($\Delta P = 2.76$ bar, $T = 50$ °C).

Gas (X)	Molecular size [a] [nm]	Molecular weight (MW)	α_{X/SF_6} [b]	Permeance [cm^3(STP)/(cm^2 s cmHg)]	α_{X/SF_6} [c]
He	0.265	4.003	6.040	3.64×10^{-3}	>2400
N_2	0.364	28.014	2.284	8.3×10^{-4}	557
C_3H_6	0.45	42.081	1.863	1.01×10^{-3}	678
SF_6	0.55	146.052	–	1.49×10^{-6}	–

[a] Kinetic diameter [23]. [b] Knudsen gas separation factors α_{X/SF_6}, calculated as $(MW_{SF_6})^{1/2}/(MW_X)^{1/2}$ [20,24]. [c] Ideal gas separation factors calculated from single gas permeation measurements.

and 350 °C, respectively. The peak at 180 °C is ascribed to the reaction of the vinyl groups in the organic templates.[21] The second peak at 350 °C was accompanied by a drastic weight loss of about 30 %, which is approximately equal to the weight percentage of the organic templates in the hybrid material. From the same figure, it is seen that, above 400 °C, there was no further appreciable weight loss up to 700 °C.

Thus the second peak is attributable to the pyrolysis of the organic templates from the hybrid xerogel[21] and the accompanying weight loss of approximately 30 % suggests that practically all of the organic templates are removed. The initial weight loss at temperatures below 250 °C (between 5 and 10 %) may be due to the removal of physically adsorbed solvents (ethanol and water) in the xerogel, which was not dried prior to the TGA/DTA experiment, along with loss of water due to continuing condensation reactions.

The xerogel pyrolyzed at 350 °C for 3 h in air (again with a weight loss of 30 %) has a characteristic type I nitrogen adsorption isotherm (as shown in Figure 2), which indicates
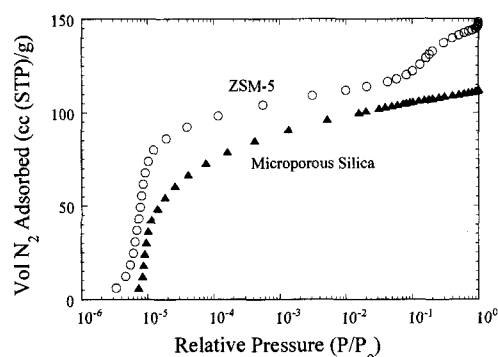

Figure 2. The nitrogen adsorption isotherm (77 K) of a bulk silica xerogel after removal of organic templates by pyrolysis at 350 °C in air for 3 h (heating rate 1 °C/min). The xerogel was prepared by co-polymerization of MPS and TEOS in a ratio of 1:4. Also included is the nitrogen adsorption isotherm (at 77 K) of the zeolite ZSM-5.

that the xerogel is microporous with pores smaller than 2 nm in diameter.[20] In a separate experiment, the xerogel was pyrolyzed at 350 °C for 6 h in oxygen; however, there was no appreciable difference observed with respect to weight loss and nitrogen sorption analysis. The above experiments suggest that the organic templates in the hybrid inorganic–organic xerogel were removed during pyrolysis at 350 °C for 3 h in air.

Comparison of the nitrogen adsorption isotherm of the porous xerogel to that of the zeolite ZSM-5 (also shown in Figure 2) indicates that both the pore size and pore size distribution in the xerogel are similar to those of ZSM-5, which has uniform pores with diameters of 0.5 nm.[22,23] The difference between pore sizes and size distributions inferred from these two nitrogen adsorption isotherms falls well within the uncertainty of the measurements. This observation implies that the xerogel, after removal of the organic templates by pyrolysis, contains pores approximately 0.5 nm in diameter (approximately the diameter of the organic ligands, based on estimates from molecular models) with a very narrow size distribution. These results further imply that the organic templates were well dispersed in the dense hybrid inorganic–organic composite and that association or phase separation of the organic ligands was not

appreciable. The experimental results above suggest that the pores in the xerogel are due to the removal of the well-dispersed organic templates from the dense, hybrid inorganic–organic composite.

Thin, hybrid, organic–inorganic films were formed by dip-coating the sols onto porous alumina tubular substrates. After the membranes had been dried at 150 °C for 3 h in air, gas permeation measurements were conducted on them. These experiments revealed that the hybrid organic–inorganic membranes were almost gas-tight, with a very small He permeance (less than $4 \times 10^{-6} \text{cm}^3$ (STP)/ $(\text{cm}^2 \text{s cmHg})$, very near the detection limit of the apparatus used). This result corroborates the nitrogen adsorption analysis and indicates that the films before pyrolysis were practically dense (i.e., free of adventitious pores). Furthermore, this result implies that the films were defect-free, i.e., there were no macroscopic pinholes or cracks. The organic templates were removed from the films by pyrolyzing the films at 350 °C for 3 h in air. Some of our single gas permeation data are summarized in Table 1 and the temperature dependence of gas permeation of various gases through the membranes is presented in Figure 3.
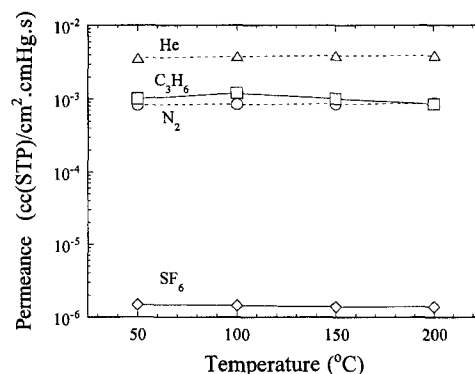

Figure 3. Gas permeance through supported, microporous silica membranes prepared by dip-coating onto mesoporous γ-alumina tubes from a diluted sol. The sol was prepared from MPS and TEOS in a ratio of 1:4. The membranes were dried in air at 150 °C for 3 h, and then subjected to pyrolysis in air at 350 °C for 3 h prior to measurements (heating rate 1 °C/min). The measurements were performed at temperatures ranging from 50 °C to 200 °C with a differential pressure across the membrane of 2.76 bar in a home-made single gas permeation apparatus.[18–19]

Both Table 1 and Figure 3 clearly indicate that the membranes are almost impermeable to SF_6, whereas He, N_2, and C_3H_6 can permeate through the membranes, although the permeances vary due to differences in the molecular weight, size, and adsorption properties of these gases.

The ideal separation factors of SF_6 from He, N_2, and C_3H_6 calculated from their respective permeances are at least 200 times larger than those expected for a Knudsen diffusion separation mechanism, as shown in Table 1; for the latter case, the separation factors are inversely proportional to the ratio of the square roots of the respective molecular weights.[20,24] Another mechanism, namely surface flow, can contribute to gas permeation through

microporous materials.[25] The high permeance of C_3H_6 relative to that of N_2 and the weak temperature dependence of the permeance (see Fig. 3) may be a result of the contribution of surface flow to C_3H_6 permeation.[25–27] A high surface flow, however, would also be expected for SF_6 (similar to C_3H_6), while surface flow would contribute less to the permeance of He and N_2.[25–27] While a detailed discussion of surface flow in microporous media is beyond the scope of this communication, the data in Figure 3 do not support these expectations and, thus, we attribute the large ideal separation factors obtained to the third mechanism of gas separation, that of molecular sieving (i.e., size exclusion) of SF_6 by the membranes. Comparison of the molecular sizes of the four probe gases reveals that only gases having a kinetic diameter smaller than or equal to 0.45 nm can permeate through the membranes. As a result, the transport of SF_6, which has a kinetic diameter of 0.55 nm, is severely restricted. Although it is expected that the gas separation factors would be infinite for a true molecular sieve, the ideal gas separation factors observed with the microporous membranes cannot be accounted for by any other separation mechanism. However, the weak temperature dependence of the permeation of He and N_2 observed in this study could not be explained satisfactorily by any mechanisms mentioned above.

It is argued that the single gas permeation measured in the present study could not be used to draw conclusions about gas separation factors of a gas mixture. Indeed, gas permeation of a mixture can be different from that of single gas systems. The interference and/or partial blocking of pathways by large molecules may result in a reduced permeance of gases composed of small molecules and, thus, reduced true gas separation factors. Our experiments on other microporous silica membranes have shown that the true gas separation factors determined from the permeation measurements of mixtures are always somewhat lower than the ideal gas separation factors calculated from single gas permeances. While it could be misleading to draw definite conclusions about gas separation properties from single gas permeation measurements, the results indicate that the microporous membranes prepared in this study consist of pores of approximately 0.5 nm diameter with a very narrow pore size distribution. Such membranes would be expected to exhibit a true molecular sieving effect. The investigation of the true gas separation properties of the microporous silica membranes prepared as described above is underway and will be reported elsewhere.

In summary, the present work demonstrates that microporous amorphous silica can be synthesized by an organic template approach using sol–gel synthesis. After heating to 150 °C a relatively dense hybrid organic–inorganic material without adventitious pores with respect to nitrogen sorption was obtained, most probably due to the presence of the organic templates and the short aging time used. After pyrolysis of the organic template ligands, both xerogels and membranes were shown to contain pores approximately

0.5 nm in diameter with a very narrow pore size distribution comparable to those of the zeolite ZSM-5. The single gas permeation measurements demonstrated that the membranes have ideal gas separation factors at least two orders of magnitude larger than those of Knudsen separation factors.

[1] Inorganic Membranes: Synthesis, Characterization and Properties (Ed: R. Bhave), Van Nostrand Reinhold, New York 1991.
[2] C. J. Brinker, G. W. Scherer, Sol-Gel Science: The Physics and Chemistry of Sol-Gel Processing, Academic Press, San Diego, CA 1990.
[3] R. L. Goldsmith, J. Membr. Sci. 1990, 39, 197.
[4] A. Larbot, J. P. Fabre, C. Guizard, L. Cot, J. Membr. Sci. 1988, 39, 203.
[5] A. F. M. Leenaars, K. Keizer, A. J. Burggraaf, J. Mater. Sci. 1984, 19, 1077.
[6] M. A. Anderson, M. J. Gieselmann, Q. Xu, J. Membr. Sci. 1988, 39, 243.
[7] T. Kokufu, T. Isoda, Japanese Patent 87/251533, A2, 1986.
[8] Y. Matsui, Y. Kikani, K. Mori, Japanese Patent 61/4513, A2, 1986.
[9] G. R. Gavalas, C. E. Megiris, S. W. Nam, Chem. Eng. Sci. 1989, 44, 1829.
[10] Y. S. Lin, A. J. Burggraaf, AIChE J. 1992, 38, 445.
[11] G. Z. Cao, H. W. Brinkman, J. Meijerink, K. J. de Vries, A. J. Burggraaf, J. Mater. Chem. 1993, 3, 1307.
[12] G. Z. Cao, H. W. Brinkman, J. Meijerink, K. J. de Vries, A. J. Burggraaf, J. Am. Ceram. Soc. 1993, 76, 2201.
[13] C. J. Brinker, R. Sehgal, S. L. Hietala, R. Deshpande, D. M. Smith, D. Loy, C. S. Ashley, J. Membr. Sci. 1994, 94, 85.
[14] R. Sehgal, C. J. Brinker, US Patent Appl. No. 08/551956, November 1995.
[15] R. S. A. de Lange, J. H. A. Hekkink, K. Keizer, A. J. Burggraaf, J. Membr. Sci. 1995, 99, 57.
[16] R. S. A. de Lange, J. H. A. Hekkink, K. Keizer, A. J. Burggraaf, J. Microporous Mater. 1995, 4, 169.
[17] N. K. Raman, C. J. Brinker, J. Membr. Sci. 1995, 105, 273.
[18] C. J. Brinker, N. K. Raman, M. N. Logan, R. Sehgal, R.-A. Assink, D.-W. Hua, T. L. Ward, J. Sol-Gel Sci. Technol. 1995, 4, 117.
[19] C. J. Brinker, T. L. Ward, R. Sehgal, N. K. Raman, S. L. Hietala, D. M. Smith, D.-W. Hua, T. J. Headley, J. Membr. Sci. 1993, 77, 165.
[20] S. J. Gregg, K. S. W. Sing, Adsorption, Surface Area and Porosimetry, Academic Press, New York 1982.
[21] IR spectroscopy conducted on the bulk, organic–inorganic composite gels at ambient temperature shows IR absorption bands characteristic of both the silicate network and organic pendant group. The IR spectra obtained after the samples were heated incrementally from ambient temperature to 600 °C support the hypothesis that the vinyl groups associated with the pendant methacryloxypropyl group are decomposed at temperatures between 150 and 200 °C. In particular, the double bond vibration at 1635 cm^{-1} diminishes in intensity and broadens. With further heating, the bands characteristic of the organic ligand are not detected at temperatures above 350 °C.
[22] M. E. Davis, Ind. Eng. Chem. Res. 1991, 30, 1675.
[23] D. W. Breck, Zeolite Molecular Sieves: Structure, Chemistry and Use, Wiley, New York 1973.
[24] E. A. Mason, A. P. Malinouskas, Gas Transport in Porous Media: The Dusty Gas Model, Elsevier, Amsterdam 1983.
[25] S. T. Hwang, K. Kammermeyer, Membranes in Separation, Techniques of Chemistry, Wiley, New York 1975, Vol. VII.
[26] E. R. Gilliland, R. F. Baddour, G. P. Perkinson, K. J. Sladek, Ind. Eng. Chem. Fundam. 1974, 13, 95.
[27] K. J. Sladek, E. R. Gilliland, R. F. Baddour, Ind. Eng. Chem. Fundam. 1974, 13, 100.