Conclusions

The SLE phase diagrams have been measured for three binary systems of heavy aromatics. These data have been used in a novel method for generating previously unknown heat of fusion data. The method can give excellent estimates for compounds forming relatively ideal solutions but is less reliable when used for systems exhibiting complex phase behavior. The experiment is relatively simple and straightforward and provides an easy evaluation of properties for unusual or difficult compounds.

Acknowledgment

we would like to acknowledge Dr. William Acree for bringing the reference to 4-hydroxybenzoic acid to our attention.

Registry No. Thianthrene, 92-85-3; salicylic acid, 69-72-7; 3-hydroxybenzoic acid, 99-06-9; phenanthrene, 85-01-8.

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Received for review March 12, 1990. Accepted June 4, 1990. We gratefully acknowledge financial support for this work from the U.S. Environmental Protection Agency, through the Advanced Environmental Control Technology Research Center at the University of Illinois, supported under Cooperative Agreement CR-806619; from the U.S. Department of Energy, under Grants DE-FG22-88PC88922 and DE-FG22-84PC70801; from the Hazardous Waster Research Information Center of the State of Illinois, under Grant SENR HWR 89-062; and for Fellowship support from Kodak, Union Carbide, General Electric, and Amoco Oil Co.

Liquid–Liquid Phase Equilibria in the Methanol + 2,2,4-Trimethylpentane and Methanol + Methylcyclopentane Systems at Pressures from 5 to 120 MPa

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Liquid–liquid phase equilibria of the mixtures methanol + 2,2,4-trimethylpentane (isooctane) and methanol + methylcyclopentane were investigated by using the synthetic method. The phase coexistence curves were determined over a pressure range from 5 to 120 MPa and a methanol mole fraction range from approximatively 0.25 to 0.85. Empirical equations were used to correlate the experimental data and to obtain the critical lines.

Introduction

The thermodynamic properties of mixtures of alcohols with hydrocarbons are of considerable theoretical interest, because they reflect effects of hydrogen bonds in a nonpolar medium. Such mixtures usually show large deviations from ideality, and hence positive azeotropy or liquid–liquid phase separations are often observed.

Phase equilibrium data for the liquid–liquid phase splitting at elevated pressures have been reported for methanol + normal alkane mixtures, as well as for ethanol + normal alkane mixtures, with the alkane carbon number ranging from 2 to 10 (*1–4*). Here, phase equilibrium data are presented for mixtures of methanol with two branched hydrocarbons in order to show the influence of molecular shape on phase behavior.

Experimental Section

The measurements were performed in a high-pressure vessel equipped with sapphire windows, as described by Liphard and Schneider (*5*), but with some modifications concerning pressure transmission, temperature regulation, and cell sealing (*6–8*). The pressure vessel was made of nonmagnetic material (Nimonic 90) in order to permit mixing with a magnetic stirrer. The vessel was filled with mixtures of known composition in the homogeneous state; then demixing was brought about by cooling at a fixed rate at constant pressure. The temperature at which the phase separation started was recorded.

The pressure was generated with a screw press and transmitted to the cell by a moving O-ring-sealed piston. Two Heise gauges, calibrated against a dead-weight gauge, were connected to the screw press. The pressure readings are estimated to be accurate to ±0.1 MPa in the range 5–80 MPa and to ±0.5 MPa above 80 MPa.

Temperatures were measured with a chromel/alumel thermocouple. Calibration of this thermocouple showed that temperature readings were accurate to ±0.03 K. The values of demixing temperatures, however, depend on the reliability of the visual detection of the phase splitting. Because the detection of a very small amount of a new phase is difficult, the accuracy of demixing temperatures is estimated to be ±0.1 K near a

Table I. Experimental Liquid–Liquid Phase Separation Temperatures T as a Function of Pressure P and Methanol Mole Fraction x

	T at various P/K							
x	5 MPa	10 MPa	20 MPa	40 MPa	60 MPa	80 MPa	100 MPa	120 MPa
			Methanol + 2,2,4-Trimethylpentane					
0.2943	307.93	309.44	310.95	314.81	318.27	321.50	323.38	325.26
0.3489	311.38	313.15	315.68	320.29	324.11	327.45	330.00	332.45
0.4257	315.17	316.96	320.00	624.89	328.94	332.61	335.90	338.79
0.5338	317.38	318.93	321.96	327.16	331.55	335.33	338.57	341.65
0.5802	318.01	319.51	322.49	327.61	331.95	335.76	339.20	342.27
0.6366	317.81	319.26	322.18	327.35	331.59	335.59	338.91	341.94
0.6679	317.94	319.45	322.44	327.57	331.88	335.71	339.15	342.22
0.7165	317.81	319.26	322.18	327.35	331.59	335.59	338.91	341.94
0.7445	317.11	318.64	321.67	326.70	331.04	334.80	338.19	341.31
0.8064	313.41	314.78	317.55	322.59	326.82	330.53	333.95	336.98
0.8504	306.48	307.65	310.27	315.17	319.25	322.83	326.05	328.92
			Methanol + Methylcyclopentane					
0.2560	298.89	300.32	302.87	307.73	311.98	315.80	319.29	322.25
0.3072	301.82	303.22	305.97	311.00	315.43	319.44	323.00	326.38
0.3464	303.12	304.57	307.61	312.76	317.23	321.40	325.01	328.41
0.4133	304.54	306.01	308.97	314.17	318.69	322.78	326.43	329.91
0.4963	304.67	306.23	309.19	314.39	318.95	323.07	326.70	330.12
0.5349	304.64	306.04	309.05	314.27	318.76	322.88	326.55	330.03
0.5612	304.57	306.09	309.10	314.34	318.83	322.98	326.63	330.08
0.6149	304.10	305.65	308.71	313.99	318.57	322.61	326.26	329.81
0.6445	303.34	304.81	307.87	313.22	317.94	322.06	325.83	329.35
0.6874	301.35	303.02	306.04	311.39	315.87	320.02	323.82	327.20
0.7189	298.79	300.32	303.32	308.26	312.78	316.75	320.38	323.48

critical point and ±0.2 K otherwise.

The filling of the pressure vessel was accomplished in two different ways:

(1) For measurements on the system methanol + 2,2,4-trimethylpentane, both components were added one after another from burets. Uncertainties of the hold-up volumes in the capillary tubes and valves limited the accuracies of the mole fractions to ±0.002.

(2) Methanol and methylcyclopentane were mixed in a gastight syringe at a temperature above the critical mixing temperature. The composition was determined by weighing and had an accuracy of ±0.0001 mole fraction unit. The homogeneous mixture was then transferred to the evacuated cell, while the inlet valves and capillaries were heated with a heating pad.

This filling method could not be used for the methanol + 2,2,4-trimethylpentane system, because its critical temperature at ambient pressure is considerably higher (316 K as compared to 303 K); such mixtures are more difficult to keep in a homogeneous state during the filling procedure.

The purities of the substances were for methanol >99.5%, for 2,2,4-trimethylpentane >99.5%, and for methylcyclopentane >99.0% (as stated by supplier).

Special precautions were taken to exclude moisture from the samples. The alkanes were stored over sodium metal and the methanol over molecular sieve (3 Å pore size). The burets were protected from moisture with drying tubes filled with P_2O_5. All transfers of chemicals were made with gas-tight syringes. The influence of moisture on the phase separation has been discussed in detail by Sieg (*9*).

Results

The phase equilibrium P, T results at various methanol mole fractions x are summarized in Table I; some of these data sets (isopleths) are also shown in Figure 1. On the right-hand side of each isopleth, only one homogeneous phase exists; the two-phase area is on the left-hand side. The curves were fitted with the Simon equation:

$$P = P_0[T/T_0]^c \tag{1}$$

P_0 and T_0 specify the reference state of this equation; these two parameters, as well as c, were calculated by nonlinear regression. The resulting values and the root-mean-square deviations are given in Table II. For the T, x isobars, the following equation was used (*1*):

Table II. Parameters for Equation 1 (Isopleths), Root-Mean-Square Deviation[a] of the Regression δP_s, and Maximum Error According to Error Analysis δP_e

x	T_0/K	P_0/MPa	c	δP_s/MPa	δP_e/MPa
		Methanol + 2,2,4-Trimethylpentane			
0.2943	306.33	548	19.19	1.399	1.515
0.3489	309.72	514	17.00	0.480	1.308
0.4257	313.67	692	13.06	0.380	1.181
0.5338	315.59	686	12.76	0.191	0.673
0.5802	316.32	787	11.75	0.090	0.671
0.6679	313.26	787	11.74	0.101	0.671
0.6366	313.06	780	11.83	0.277	0.672
0.7165	316.06	780	11.83	0.277	0.672
0.7445	315.47	789	11.78	0.168	1.147
0.8064	311.76	863	11.21	0.178	1.208
		Methanol + Methylcyclopentane			
0.2560	297.35	991	9.84	0.310	1.169
0.3072	300.27	1089	8.91	0.120	1.123
0.3464	301.50	980	9.35	0.190	1.100
0.4133	302.94	1017	9.15	0.160	0.648
0.4963	303.06	966	9.45	0.100	0.647
0.5349	303.01	1024	9.09	0.200	0.647
0.5612	302.96	978	9.35	0.170	0.646
0.6149	302.49	955	9.44	0.290	1.088
0.6445	301.64	974	9.14	0.160	1.074
0.6874	299.77	939	9.40	0.230	1.083
0.7189	297.17	879	9.99	0.230	1.122

[a] Definition of the root mean square deviation: $\delta P_s = [(1/N)\sum_i^N(P_i^{exp} - P^{calc}(T_i^{exp}))]^{0.5}$, where the summation extends over N data sets (T_i^{exp}, P_i^{exp}) and P^{calc} is the function defined by eq 1.

$$T = T_c - k|y - y_c|^n \tag{2}$$

with

$$y = \frac{\alpha x}{1 + x(\alpha - 1)} \quad \text{and} \quad y_c = \frac{\alpha x_c}{1 + x_c(\alpha - 1)}$$

Here, T_c and x_c denote respectively the upper critical mixing temperature and the critical mole fraction; α, n, and k are adjustable parameters. The coefficients of eq 2 and the

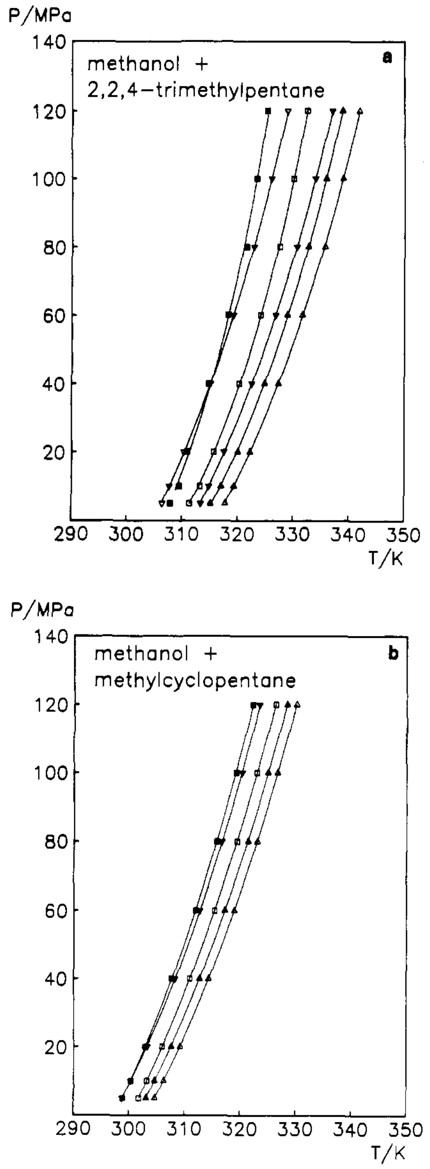

Figure 1. Liquid-liquid phase separation pressure P against temperature T at constant methanol mole fraction x. Points, experimental data; curves, calculated, eq 1 (Simon equation) with parameters from Table II (not all data from Table I are shown to avoid cluttering). (a) Methanol + 2,2,4-trimethylpentane: ■, $x = 0.2943$; □, $x = 0.3489$; ▲, $x = 0.4257$; △, $x = 0.6366$; ▼, $x = 0.8064$; ▽, $x = 0.8504$. (b) Methanol + methylcyclopentane: ■, $x = 0.2560$; □, $x = 0.3072$; ▲, $x = 0.3464$; △, $x = 0.4963$; ▼, $x = 0.7189$.

root-mean-square deviations of the regression are given in Table III. The isobars are shown in Figure 2.

For the assessment of errors it is necessary to recall that the phase boundary is detected visually when it is crossed, i.e. the contents of the pressure cell become turbid because of the precipitation of a new phase. In order to form detectable amounts of the new phase, however, it is necessary to move slightly into the two-phase area. The observed equilibrium temperatures are therefore systematically too low; this effect is negligible near a critical point, but may become important farther away.

The experimental uncertainties of equilibrium temperatures and pressures, which are reported in Tables II and III, are combinations of instrument errors (δT_i, δP_i, δx_i) and detection errors. The latter are assumed to be proportional to the slope of the phase boundary. Therefore, the experimental errors are estimated by

$$\delta T_e = \left|\frac{dT}{dx}\right|\delta x_i + \delta T_i \qquad \delta P_e = \left|\frac{dP}{dT}\right|\delta T_e + \delta P_i \qquad (3)$$

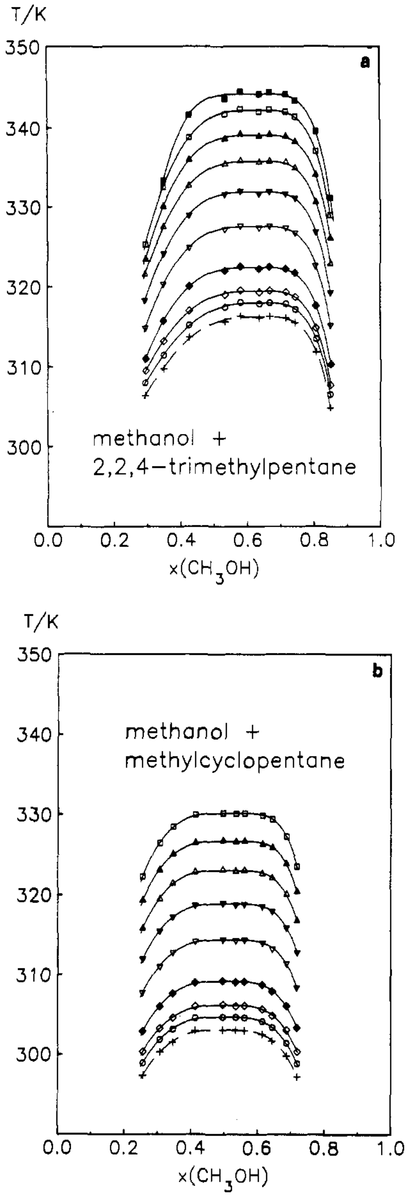

Figure 2. Liquid-liquid phase separation temperature T against methanol mole fraction x at constant pressure P. Points, experimental data; curves, calculated, eq 2 with parameters from Table II. (a) Methanol + 2,2,4-trimethylpentane: ○, $P = 5$ MPa; ◇, $P = 10$ MPa; ◆, $P = 20$ MPa; ▽, $P = 40$ MPa; ▼, $P = 60$ MPa; △, $P = 80$ MPa; ▲, $P = 100$ MPa; □, $P = 120$ MPa; ■, $P = 140$ MPa; +, $P = 0.1$ MPa (extrapolated). (b) Methanol + methylcyclopentane: ○, $P = 5$ MPa; ◇, $P = 10$ MPa; ◆, $P = 20$ MPa; ▽, $P = 40$ MPa; ▼, $P = 60$ MPa; △, $P = 80$ MPa; ▲, $P = 100$ MPa; □, $P = 120$ MPa; ■, $P = 140$ MPa; +, $P = 0.1$ MPa (extrapolated).

where the instrument error are assumed to be $\delta x_i = 0.002$ for 2,4,4-trimethylpentane, $\delta x_i = 0.0001$ for methylcyclopentane, $\delta P_i = 0.1$ MPa for 5 MPa $< P <$ 80 MPa, $\delta P_i = 0.5$ MPa for $P >$ 80 MPa, $\delta T_i = 0.1$ K in the critical region (0.5-0.65 for 2,2,4-trimethylpentane, 0.35-0.62 for methylcyclopentane), and $\delta T_i = 0.2$ K elsewhere.

Discussion

As shown in Figure 1, the P, T isopleths run monotonously to higher temperatures and pressures with increasing slopes. The critical line, which is defined as the envelope of the set of isopleths, is almost indistinguishable from the right most isopleth. Evidently, the critical mole fraction does not change very much along the critical line. The critical points forming this line are upper critical solution points. Together with the positive slope of the critical line, this indicates positive excess enthalpies and

Table III. Parameters for Equation 2 (Isobars), Root-Mean-Square Deviation of the Regression δT_s, and Maximum Error According to Error Analysis δT_e[a]

P/MPa	T_c/K	x_c	n	k/K	α	δT_s/K	δT_e/K
			Methanol + 2,2,4-Trimethylpentane				
5	317.94 ± 0.13	0.638 ± 0.005	3.28	737	0.399	0.097	0.158
10	319.41 ± 0.13	0.633 ± 0.005	3.44	890	0.424	0.104	0.159
20	322.37 ± 0.15	0.626 ± 0.006	3.66	1200	0.489	0.118	0.164
40	327.51 ± 0.13	0.625 ± 0.005	3.70	1313	0.516	0.098	0.168
60	331.83 ± 0.13	0.627 ± 0.005	3.70	1314	0.513	0.102	0.168
80	335.71 ± 0.11	0.628 ± 0.004	3.61	1270	0.515	0.089	0.169
100	339.07 ± 0.15	0.628 ± 0.005	3.71	1499	0.532	0.116	0.174
120	342.13 ± 0.14	0.629 ± 0.005	3.75	1653	0.542	0.114	0.177
			Methanol + Methylcyclopentane				
5	304.67 ± 0.08	0.506 ± 0.004	3.27	778	0.701	0.052	0.172
10	306.16 ± 0.11	0.509 ± 0.006	3.30	830	0.670	0.079	0.169
20	309.15 ± 0.09	0.510 ± 0.005	3.40	990	0.689	0.066	0.171
40	314.36 ± 0.10	0.516 ± 0.005	3.59	1470	0.625	0.074	0.167
60	318.88 ± 0.09	0.518 ± 0.004	3.72	1911	0.594	0.062	0.166
80	322.99 ± 0.10	0.518 ± 0.005	3.83	2321	0.602	0.071	0.166
100	326.63 ± 0.11	0.523 ± 0.005	3.97	3133	0.558	0.078	0.165
120	330.09 ± 0.07	0.523 ± 0.003	4.15	4504	0.547	0.051	0.165

[a] Error margins of T_c and x_c are statistical uncertainties of the nonlinear regression. Definition of the root mean square deviation: $\delta T_s = [(1/N)\sum_i^N(T_i^{exp} - T^{calc}(x_i^{exp}))]^{0.5}$, where the summation extends over N data sets (x_i^{exp}, T_i^{exp}) and T^{calc} is the function defined by eq 2.

Table IV. Upper Critical Mixing Temperatures T_c and Methanol Mole Fractions x_c at Pressure P = 0.1 MPa for Several Methanol + Alkane Mixtures[a]

alkane	T_c/K	x_c	ref
butane	266.45	0.3990	3
pentane	286.92	0.4966	3
cyclopentane	289.75	(0.45)	10
hexane	307.25	0.535	2
cyclohexane	318.90	(0.50)	10
3-methylpentane	300.35	(0.50)	10
methylcyclopentane	303.06	0.5048	this work
heptane	324.50	0.590	1
2,2,3-trimethylbutane	301.35	(0.58)	9
methylcyclohexane	319.15	(0.55)	10
octane	339.30	0.639	1
3-methylheptane	333.35	(0.63)	10
2,2,4-trimethylpentane	316.20	0.6372	this work

[a] Values in parentheses were taken from diagrams and must be regarded as less accurate.

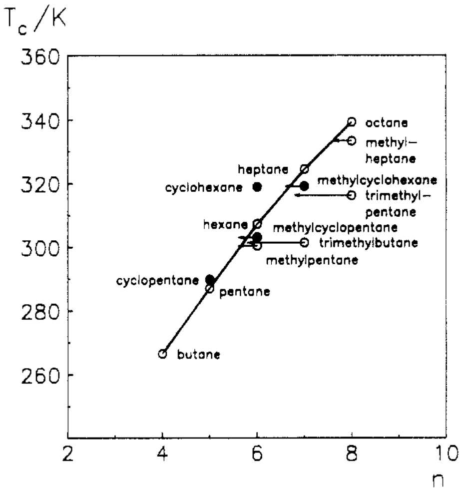

Figure 3. Critical mixing temperatures T_c of methanol + alkane mixtures at ambient pressure plotted against the number n of carbon atoms in the alkane: O, normal and iso alkanes; ●, cycloalkanes. The bold line connects the points representing the normal alkanes. The arrows point to locations for branched hydrocarbons, if methyl groups in iso position are assumed to contribute only 0.6 to the carbon number n.

excess volumes, as can be expected for mixtures of a polar with a nonpolar component under such conditions.

It is interesting to compare the recent results for 2,2,4-trimethylpentane and methylcyclopentane with those for other alkanes. Table IV contains critical temperatures and mole fractions at ambient pressure for several methanol + alkane mixtures. It must be noted that in several cases the data had to be read off a diagram and are not very accurate; such data are marked with brackets. Since the lowest pressure used in this work was 5 MPa, the experimental data had to be extrapolated down to 0.1 MPa. This was done with the Simon equation (eq 1). In addition, the critical solution temperatures have been plotted against the alkane carbon numbers in Figure 3.

It has long been known that for methanol + *n*-alkane mixtures the critical solution temperature and the critical mole fraction increase with the carbon number. A comparison with the entries for cyclopentane and cyclohexane shows that their critical points are very close to those of pentane and hexane. One might conclude that the difference in flexibility between cyclo- and *n*-alkanes contributes little to the thermodynamic properties. The isoalkanes, however, deviate markedly from their straight-chain homologues. It seems that a methyl group in an iso position contributes much less to the molecular size and interaction pair potential than a methyl group at the end of a chain. Indeed, the critical temperatures of methanol + isoalkane mixtures can be obtained by linear interpolation of the *n*-alkane entries in Table IV or Figure 3, if methyl groups in iso positions are assumed to contribute only 0.6 to the total carbon number.

Once this correction to the carbon number is applied, the substance showing the largest departure from the *n*-alkane data is cyclohexane. However, cyclohexane has a—for a hydrocarbon of this size—very high melting point and an unusually large liquid density. One might conclude that cyclohexane molecules are packed with a higher efficiency and with a different degree of short-range order than other hydrocarbon molecules of less symmetry. A quantitative discussion of this problem is beyond the scope of this work.

The slope dP/dT of the critical line of 2,2,4-trimethylpentane, as well as that of methylcyclopentane, is about 3.3 MPa/K in the low-pressure limit. This is slightly higher than, but still very close to, the typical value for the methanol + alkane "family" (3.1 MPa/K), which can be obtained from literature data for methanol + *n*-alkane systems under pressure (*1*–*8*). At high pressures, however, the different molecular shapes become important: At about 100 MPa the *n*-alkane mixtures have slopes between 5.3 MPa/K (decane) and 6.4 MPa/K (butane);

for heptane the value is about 5.9 MPa/K. 2,2,4-Trimethylpentane shows a significantly higher value (6.5 MPa/K), whereas methylcyclopentane is close to the heptane value. Evidently, high-pressure phase equilibria are more sensitive to differences in molecular structure than equilibria at ambient pressure.

Acknowledgment

We thank Prof. Dr. G. M. Schneider (Lehrstuhl für Physikalische Chemie II, Ruhr-Universität Bochum) for permission to use the experimental equipment of his institute.

Registry No. Methanol, 67-56-1; 2,2,4-trimethylpentane, 540-84-1; methylcyclopentane, 96-37-7.

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Received for review January 18, 1990. Accepted June 12, 1990. Financial support by the Fonds der Chemischen Industrie e.V. and by the Winnacker-Stiftung is gratefully acknowledged.

Thermodynamic Equilibrium of Diluted SO_2 Absorption into Na_2SO_4 or H_2SO_4 Electrolyte Solutions

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An investigation of the thermodynamics of SO_2 absorption into aqueous sulfate or sulfuric acid solutions is reported. The study has been conducted on SO_2 scrubbing under industrial practice and its possible further oxidation into sulfate compounds. Low-cost electrolytes—sodium sulfate or sulfuric acid—have been considered below 2 M, and the flue-gas partial pressure was varied between 10^{-4} and 0.1 atm. Temperatures were fixed at 25 and 50 °C. Available data relative to SO_2 solubility in the selected electrolytes were surveyed. The results, obtained by the theoretical approach, have been expressed in the form of the pH evolution vs the total amount of tetravalent sulfur, present either in molecular or ionized form, which still has to be converted through a further process, i.e. electrochemical or chemical. The performance of the various models proposed for the estimation of activity coefficients is discussed in this paper; for the parameter ranges investigated here, most calculations could be carried out with a sufficient accuracy with the help of the "macroscopic" relations suggested by Meissner or Bromley. Experimental saturation of electrolyte solution with diluted SO_2 could validate the models used.

Introduction

SO_2 absorption is of major interest for solving pollution problems arising predominantly in industrial areas and represents therefore an important domain of technological interest. Sulfur dioxide can be scrubbed, for example, into molten salts at fairly high temperature or dissolved into various kinds of electrolytes. Among the various existing processes of mentionable relevance in the literature are some which involve a further treatment of dissolved sulfur dioxide through chemical oxidation (see for instance the papers of Goto and Smith (*1*) or Berrutti et al. (*2*)) or via an electrooxidation process (*3*, *4*). This oxidation of the dissolved sulfur dioxide yields sulfate ions, which, depending on the nature of the process, can lead either to dilute or highly concentrated sulfuric acid. In order to reduce the number of species present in the saturated electrolyte, one can make use of sulfate compounds, on one hand, as an absorption medium and, on the other hand, as a supporting electrolyte. Therefore, sodium sulfate and sulfuric acid can be selected for scrubbing media. Moreover, the moderate cost of such a supporting electrolyte is an additional criterion for the feasibility of an industrial scale process for flue-gas desulfurization.

The present work concerns thermodynamic aspects of the absorption of SO_2-containing flue gas produced by industrial operations. The overall pressure is close to 1 atm, and the simulated pollutant mole fraction is varied from low concentrations up to concentrations of several percent. For the sake of the design and mounting of an oxidizing scrubber installation, the maximal amount of pollutant to be converted can be attained through the thermodynamics of the system SO_2/electrolyte. SO_2 is a fairly strong acid and when dissolved in aqueous medium, can dissociate into HSO_3^- and SO_3^{2-}. The extent of both dissociations is a function of the pH of the electrolyte. Thus, the further treatment of the dissolved flue gas will largely depend on the overall amount of sulfur dioxide already absorbed in the liquid phase, present either in molecular or ionized form. This study has been conducted to render available a data source useful in the removal of sulfur dioxide through a chemical or electrochemical operation; it allows the prediction of the chemical composition of sulfate solutions saturated with sulfur dioxide under various operating conditions.

In a general manner, dissolution of the considered flue gas into sulfate electrolytes is accompanied by the partial dissociations of both sulfur dioxide and the supporting electrolyte. The saturated electrolyte containing a numerous amount of important chemical species involves a fairly complex thermodynamical approach, differing significantly from the more pure and academic manner taken into consideration up to now. The thermodynamics of the systems $SO_2/H_2O/H_2SO_4$ and $SO_2/H_2O/Na_2SO_4$ does not seem to have been studied previously. Experimental data of SO_2 solubility in various sulfate electrolytes (*5*) or theoretical work for the system SO_2/H_2O (*6*, *7*) exists in relevant literature publications for which realistic models for

0021-9568/90/1735-0453$02.50/0