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Literature Cited

(1) Harney, B. M.; Mills, A. G. *Hydrocarbon Process.* **1980**, *59*, 67.
(2) Chang, C. D.; Silvestri, A. J. *J. Catal.* **1977**, *47*, 249.
(3) Streett, W. B.; Calado, J. C. G. *J. Chem. Thermodyn.* **1978**, *10*, 1089.
(4) Tsang, C. Y.; Clancy, P.; Calado, J. C. G.; Streett, W. B. *Chem. Eng. Commun.* **1980**, *6*, 365.
(5) Tsang, C. Y.; Streett, W. B. *Chem. Eng. Sci.*, in press.
(6) Tsang, C. Y.; Streett, W. B. *Fluid Phase Equilib.*, in press.
(7) Streett, W. B.; Erickson, A. L. *Phys. Earth Planet. Inter.* **1972**, *5*, 357.
(8) Winkler, C. A.; Maass, O. *Can. J. Res.* **1932**, *6*, 458.
(9) Joffe, J.; Zudkevitch, D. *Ind. Eng. Chem. Fundam.* **1966**, *5*, 455.
(10) Peng, D. Y.; Robinson, D. B. *Ind. Eng. Chem. Fundam.* **1976**, *15*, 159.
(11) Deiters, U. Ph.D. Thesis, Bochum University, West Germany, 1979; *Chem. Eng. Sci.*, in press.
(12) Carnahan, N. F.; Starling, K. F. *J. Chem. Phys.* **1969**, *51*, 635.
(13) Braker, W.; Messman, A. L. "Matheson Gas Data Book", 5th ed.; The Matheson Co.: E. Rutherford, NJ, 1971.

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Solubility of Chlorine in Benzene, Toluene, Ethylbenzene, *o*-, *m*-, and *p*-Xylenes, and 2-, 3-, and 4-Chlorotoluenes

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The solubilities of chlorine were measured in benzene, toluene, ethylbenzene, *o*-, *m*-, and *p*-xylenes, and monochlorinated toluenes at temperatures from 15 to 75 °C. A standard titration technique was used. The temperature dependency of the solubilities follows van't Hoff's equation. The heat of solution varies from 31 kJ/mol for benzene to 17 kJ/mol for xylene.

Introduction

There are many industrially important reactions which are carried out in multiphase systems. In such reaction systems, solubilities are fundamental data which are urgently needed for reliable design and scale-up purposes. Among the reactions carried out in gas-liquid reactors, chlorinations are widespread. It is therefore surprising that only a few solubility data are available for chlorine in aromatic compounds and their chlorinated derivatives (*1-4*). This communication presents new data on the solubility of chlorine in benzene, toluene, *o*-, *m*-, and *p*-xylenes, ethylbenzene, and the monochlorinated toluenes.

Experimental Section

The chlorination of alkylated aromatic compounds and their chloroderivatives proceeds fairly slowly in the dark but is substantially accelerated by visible light. Therefore, the measurements were carried out under conditions which prevented access of light, and, in addition, ~1% of phenol was added as an inhibitor.

The solubilities of chlorine were measured in a stirred cell, the design of which is shown in Figure 1. The all-glass cylindrical vessel had 6-cm i.d. and a height of 11 cm. It was enclosed in a thermostatic jacket and equipped with a reflux condenser, a gas inlet, and a sample tube. The whole vessel was wrapped in aluminum foil to suppress photochemical chlorination. Chlorine was taken from a cylinder and dried with sulfuric acid before being sparged into the liquid in the vessel. After the chlorine was sparged for 0.5 h under vigorous stirring, saturation was completed. Liquid samples were withdrawn by means of a sampling tube connected to the vessel (see Figure 1).

The chlorine content was analyzed by an iodine-displacement method similar to that used by Silberstein (*3*) and Le Page (*5*). The sample was injected into a certain volume of the corresponding aromatic, and then 250 mL of 0.5 N KI solution was added to the diluted sample. The liberated iodine is titrated with a standardized solution of $Na_2S_2O_3$.

The chlorine solubility in mol/L at a partial pressure of chlorine of 760 torr is calculated from eq 1, where N is the normality of $Na_2S_2O_3$ solution, V_T is the volume of $Na_2S_2O_3$ solution added, V_S is the sample volume, and P_{Cl_2} is the partial pressure of Cl_2 which is given by the barometric pressure P_B and the partial pressure of the solvent P_S; i.e.

$$c = \frac{NV_T}{2V_S}\,\frac{760}{P_{Cl_2}} \qquad (1)$$

$$P_{Cl_2} = P_B - P_S \qquad (2)$$

Results

The measured chlorine solubilities in the various aromatics for the temperature range of 15-75 °C are listed in Table I. Each value represents an average of three or four measurements. The mean relative error is less than 0.5%.

In Figures 2 and 3, log c is plotted vs. $1/T$. Straight lines were found; hence, the solubility of chlorine in the aromatics applied obeys van't Hoff's equation, i.e.

$$\log \frac{c(T_2)}{c(T_1)} = \frac{\Delta_S H}{2.303R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) \qquad (3)$$

The heats of solution were obtained from least-squares fits and are given in Table I. The value of $\Delta_S H$ for toluene found in this study is in fair agreement with that of -23 kJ/mol assumed by Shah (*6*). Figure 4 compares the results of this study with data available from the literature. In the case of benzene, the

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Table I. Solubilities of Chlorine (c)[a] and Heats of Solution

T, °C	benzene	toluene	ethylbenzene	p-xylene	o-xylene	m-xylene	2-chloro-toluene	3-chloro-toluene	4-chloro-toluene
15	3.590	2.570	2.193	1.693			2.306		
25	2.521	1.905	1.657	1.397	1.373		1.745	1.398	1.386
35	1.780	1.479	1.228	1.127		1.124	1.311	1.180	
45	1.110	1.122	0.980	0.921	0.915		1.036	0.940	0.884
55	0.841	0.771	0.779	0.767		0.765	0.842		0.741
65	0.503	0.611	0.660	0.623	0.627		0.674	0.624	0.552
75		0.464	0.528	0.484			0.547	0.499	0.479
heat of soln, ($-\Delta_S H$), kJ/mol	31.36	23.97	19.70	17.10			19.87	18.00	18.40

[a] In mol of Cl_2/L at a partial pressure of chlorine of 760 torr.

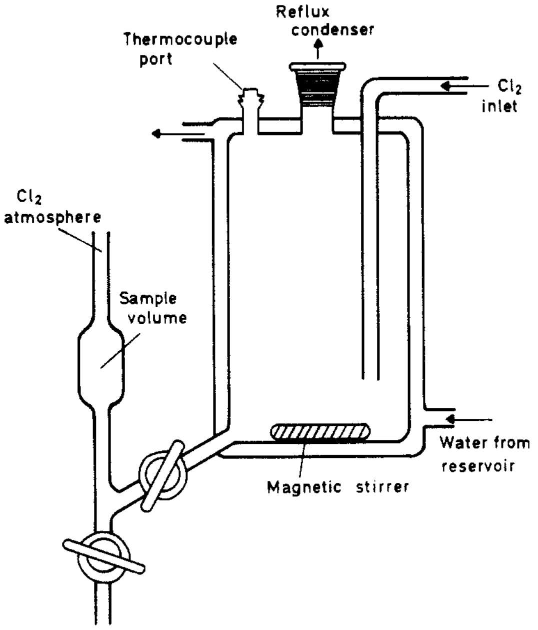

Figure 1. The stirred cell.

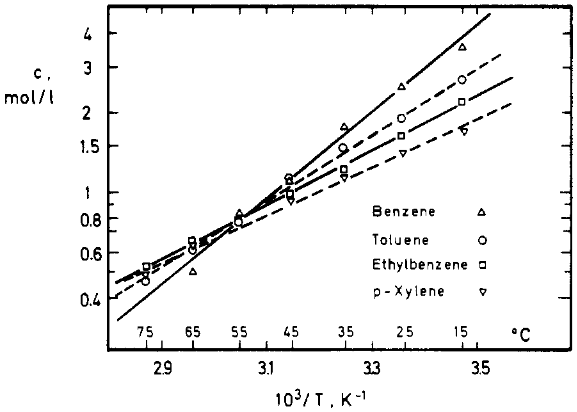

Figure 2. Temperature dependency of chlorine solubility.

agreement with the results of Krivonos (*1*) is rather good, while the value reported by Rathjen (*4*) for 20 °C is considerably larger. Also, for Cl_2 solubility in toluene, the present data are in accordance with those of Egunov et al. (*2*).

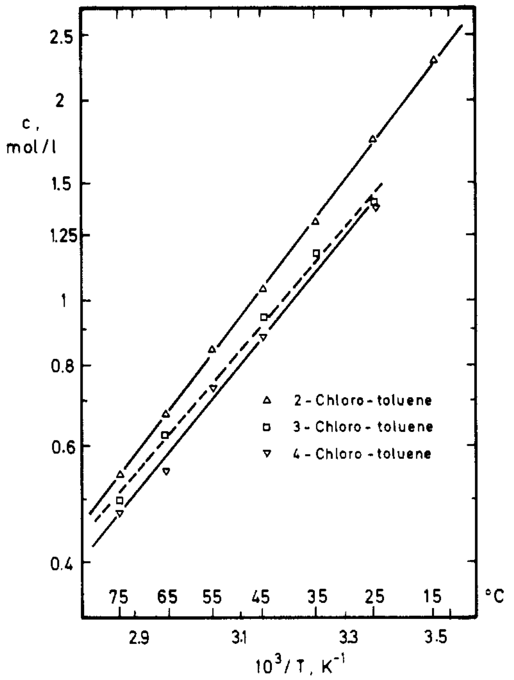

Figure 3. Temperature dependency of chlorine solubility.

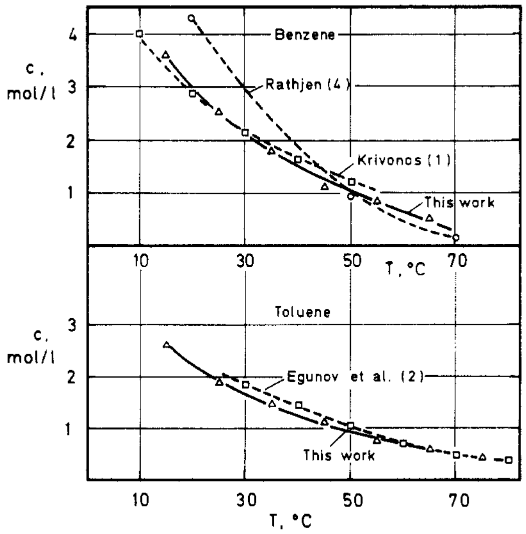

Figure 4. Comparison of Cl_2 solubilities of this study with literature data.

Glossary

c	solubility of chlorine, mol/L
$\Delta_S H$	heat of solution, kJ/mol
V_T	volume of sodium thiosulfate solution, mL
V_S	sample volume, mL
R	gas constant, 8.314 J/(mol K)
P_{Cl_2}	partial pressure of chlorine, torr
P_B	barometric pressure, torr
P_S	partial pressure of the solvent, torr
T	temperature, K (or °C in Figure 4)

Literature Cited

(1) Krivonos, F. F. *Zh. Prikl. Khim.* **1958**, *31*, 300.

(2) Egunov, A. V.; Konobeev, B. I.; Tyabov, E. A.; Gubanova, T. I. *Zh. Prikl. Khim.* **1973**, *46*, 1855.

(3) Silberstein, B.; Bliss, H.; Butt, J. B. *Ind. Eng. Chem. Fundam.* **1969**, *8*, 366.

(4) Rathjen, H. In "Ullmann: Enzyklopädie der technischen Chemie": Urban & Schwarzenberg: Müchen, 1959; Vol. 9, p 506.

(5) LePage, J.; Jungers, J. C. *Bull. Soc. Chim. Fr.* **1960**, 525.

(6) Shah, Y. T.; Szeri, A. Z. *Chem. Eng. Sci.* **1974**, *29*, 2219.

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Adsorption of a Gaseous Mixture of Ethane and Propane on a Carbon Molecular Sieve

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The adsorption of a binary gaseous mixture of ethane and propane on the carbon molecular sieve MSC·5A was measured at temperatures of 5, 30, and 50 °C and a pressure of 100 mmHg and at 30 °C and 300 mmHg. The amount of propane adsorbed was much higher than the value predicted by the method of Myers and Prausnitz. This preference for propane was greater at lower temperatures but did not change with pressure. Activity coefficients of the adsorbed phase calculated by the Myers–Prausnitz method showed that, at very high concentrations of propane, ethane dissolved in the adsorbed propane in the micropores rather than adsorbed on the surface of the adsorbent.

In a previous paper (*1*) we reported adsorption equilibrium data of pure light hydrocarbons on a hydrophobic microporous adsorbent, the carbon molecular sieve MCS·5A. Its physical and surface properties were reported in the same paper.

Since the adsorption of mixtures in the micropores deviates much from the value predicted by using the pure-component isotherms, it is necessary to generate experimental data for the development of correlations and predictions of mixture adsorption. In this paper we report the adsorption equilibrium data for the ethane–propane–MCS·5A system at 5, 30, and 50 °C and 100 mmHg, and also at 30 °C and 300 mmHg. The experimental data were compared with the values predicted by the method of Myers and Prausnitz (*2*) and of Cook and Basmadjian (*3*). The activity coefficients of ethane and propane in the adsorbed phase, which was obtained by the Myers–Prausnitz method, gave information about the behavior of the adsorbed phase in the micropores.

Experimental Section

The experimental apparatus was basically volumetric, but it has a spring balance in the adsorption tube in order to measure the weight of adsorbent after the degassing and to obtain the total weight of adsorption. The apparatus is shown in Figure 1. The volume of the adsorption tube including the capillary line was measured by helium and was found to be 668.70 (5 °C), 673.65 (30 °C), and 674.60 mL (50 °C). This size of volume was satisfactory for the equilibria not to be perturbed when 2 mL of the gas sample was taken 4 or 5 times for the gas-chromatographic analysis. In order to prepare the gas mixture, we measured propane in the gas buret whose temperature was held constant by circulating water. The gas was then let into the high-pressure gas cylinder which was cooled by the liquid nitrogen. Propane was thus frozen in the cylinder. The second component, ethane, was led into the same cylinder by the same procedure. The liquid-nitrogen bath was then removed and the cylinder was left at room temperature for 24 h to make the contents reevaporate and mix completely. The ~450 mg of adsorbent was degassed at 360 °C under high vacuum for 2 h. The weight of the sample was measured by deflection of a spring balance whose sensitivity was 0.023 97 cm/mg.

The preestimated gas mixture was introduced into the gas buret, and cock A was opened to let the gas into the adsorption tube, while the mercury level was elevated to adjust to the equilibrium pressure of ca. 100 mmHg. After the adsorption proceeded by 80~90% (20~30 min), the pressure was adjusted again to 100 mmHg. Cock A was then closed, and the remaining gas in the buret was evacuated. The mercury level was again elevated to the top line of the buret in order to minimize the volume. Since this minimum volume of the capillary tubing was 4.11 mL, no serious pressure change would occur when cock A was reopened. Ca. 24 h were necessary for the attainment of the adsorption and gas-phase equilibrium. The final equilibrium pressure was read by the manometer, and the total weight of adsorption was known by the spring balance. The gas composition was analyzed by gas chromatography, and the adsorption amount of each component was calculated from the material balance.

The total amounts of adsorption obtained by the material balance were greater than those obtained by the spring balance by 0~5%, depending on the temperature and the composition. Since this discrepancy could be attributed to the adsorption on the system, such as the lubricant of the stopcocks and the joints, and the inside surface of the apparatus, the total weight of adsorption measured by the spring balance was considered to be the true value. The adsorption of pure ethane and propane on the apparatus system was obtained at each temperature and at 100 mmHg. Since these values had rather a poor reproducibility because of the different behavior of lubricant at each run, the adsorbed weight ratios of propane to ethane on the apparatus were used; they were 2.3 (5 °C), 4.1 (30 °C), and 6.3 (50 °C). These values are close to the solubility ratio of propane to ethane in benzene, which is 3.90 at 20 °C (*4*).

The adsorption on the apparatus from the mixture was regarded as the mole fraction linear average. The amounts of each component adsorbed on the apparatus a_i are therefore expressed by eq 1 and 2, where L is the adsorbed weight ratio

$$a_1 \text{ (ethane)} = \Delta W Y_1/(Y_1 + Y_2 L) \qquad (1)$$

$$a_2 \text{ (propane)} = \Delta W Y_2 L/(Y_1 + Y_2 L) \qquad (2)$$

of propane to ethane, the values of which are given above, and

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