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Vapor-Liquid Equilibria of Methane-Benzene, Methane-Methylbenzene (Toluene), Methane-1,3-Dimethylbenzene (*m*-Xylene), and Methane-1,3,5-Trimethylbenzene (Mesitylene) at 313.2 K up to the Critical Point

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A static method, described in a previous article, has been used to perform high-pressure vapor-liquid equilibria up to the critical point on methane-aromatic hydrocarbon systems. Comparisons with literature data are presented. New data are given for the systems methane-*m*-xylene and methane-mesitylene.

Introduction

Methane solubility in hydrocarbons is a very important property for optimization of tertiary oil recovery processes by miscible gas drive. The data on many methane-hydrocarbon binary systems were already reported, but new measurements up to the critical point are needed to determine the influence of the chemical nature and degree of branching of the hydrocarbon upon vapor-liquid equilibria. Here the degree of substitution of methyl groups for hydrogen on the benzene ring is considered, and the data of several authors are compared to present data to establish a basis for choice of the most reliable experimental method and source of data.

Experimental Section

Apparatus. The experimental setup described in a previous paper (1) is based on a static method. The equilibrium cell with an internal capacity of 100 cm³ is kept at constant temperature (± 0.25 K) in an air thermostat. Pressure measurements inside the cell are obtained within 10⁵ Pa through a pressure transducer (BLH type GPH 0-1380 $\times 10^5$ Pa) calibrated at the equilibrium temperature against a dead-weight gauge (Budenberg type 280 H). The temperature is read through calibrated thermocouples within 0.2 K. The mixture is vigorously stirred by means of a small magnet rotating in a magnetic field induced by four solenoids located outside the cell.

Sampling of both phases is achieved by using two microcells the internal volumes of which are less than 15 μ L. Analysis of the samples is performed by gas chromatography using an original injection port assembly. This original sampling method associated with gas-chromatography analysis is especially suitable for study of mixtures at equilibrium temperatures lower

Table I. Density and Refractive Index of Liquid Components

	refractive index at 293.15 K		density at 293.15 K	
	this work	lit. values (15)	this work	lit. values (15)
benzene	1.5012 ₆	1.501 12	0.8791 ₇	0.8790
toluene	1.4969 ₁	1.496 93	0.8669 ₈	0.86696
<i>m</i> -xylene	1.4975 ₈	1.497 22	0.8643 ₄	0.86417
mesitylene	1.4995 ₂	1.499 37	0.8653 ₃	0.8653

Table II. Vapor-Liquid Equilibrium Data for the System Methane (1)-Benzene (2) at $T = 313.2$ K

10 ⁻⁵ P, Pa	x_1	y_1	K_1	K_2
36.6	0.0986	0.987 ^a	10.01	0.014
36.6		0.987		
101.0	0.210	0.987 ^a	4.70	0.016 ₅
101.0	0.212		4.66	
148.7	0.287	0.986	3.44	0.020
148.7	0.288		3.42	
199.8	0.369	0.984 ^a	2.67	0.025
199.8	0.367		2.68	
250.3	0.442	0.977	2.21	0.041
250.3	0.439		2.23	
310.4	0.521	0.951	1.83	0.102
351.1	0.593	0.883	1.49	0.287
351.1	0.586		1.51	0.283
368.7	0.661	0.836	1.27	0.47
368.7		0.840		0.48
374.2	0.688	0.801	1.16	0.64
374.2		0.805	1.17	0.63

^a Interpolated values.

than the boiling point of one or several components. Mean accuracies have been estimated within 0.01 for liquid mole fractions and 0.005 for vapor mole fractions.

Chemicals. Methane was supplied by Air-Gas with a specified minimum purity of 99.95 vol %. Benzene, toluene, and *m*-xylene were purchased from Merck with reported GLC purities of 99.7%, 99.5%, and 98.5%, respectively. The impurities contained in *m*-xylene were *o*-xylene (0.5%), *p*-xylene (0.5%), and ethylbenzene (0.5%). Mesitylene was obtained

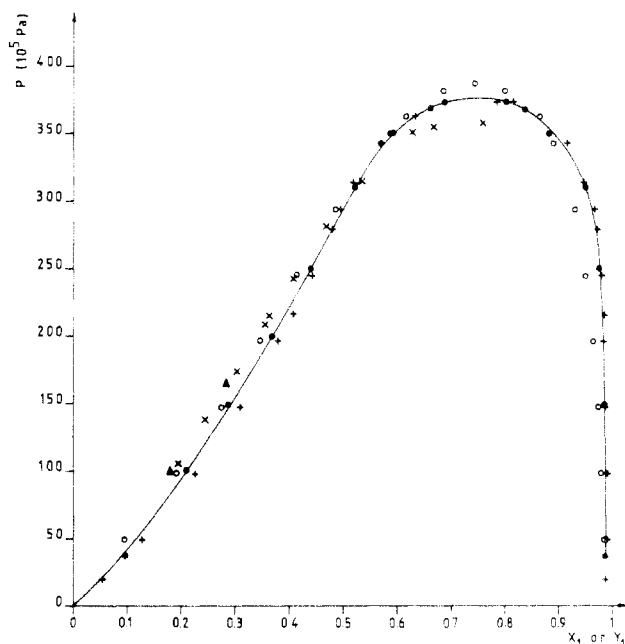


Figure 1. Vapor-liquid equilibrium data for the system methane (1)-benzene (2): (●) 313.2 K isotherm (present work), (+) 313.15 K isotherm (ref 3-5), (○) 313.15 K isotherm (ref 7), (×) 311.08 K isotherm (ref 6), (▲) 310.95 K isotherm (ref 8).

from Fluka with a guaranteed purity of not less than 99%. These components have been used without any further purification. For each liquid component, refractive index (vapor sodium lamp) and density (Anton Paar densimeter model DMA 50 W) are reported at 293.15 K in Table I.

Results and Discussion

Methane-Benzene. Our results are reported in Table II. The pressure, $P = 36.6 \times 10^5$ Pa, corresponding to the liquid mole fraction $x_1 = 0.0986$ was determined by M eskel-Lesavre with a static apparatus using a variable-volume cell (2). This value is in good agreement with our results. This system has been previously studied by several authors (3-8). There is considerable disagreement among their data. Maximum deviations are 0.05 for liquid mole fractions, 0.035 for vapor mole fractions and 30×10^5 Pa for the critical pressure. Figure 1 shows that the present data are in best agreement with Savvina et al. (3-5) after conversion of K_i values into mole fractions x_i and y_i . The critical pressure at 313.2 K was found to be $(378 \pm 2) \times 10^5$ Pa. Schoch (6) reports 360×10^5 Pa at $T = 311$ K with an apparatus using a variable-volume cell, which seems inappropriate to perform measurements in the critical region. Stepanova et al. (7) give 387.4×10^5 Pa for the critical pressure at $T = 313.15$ K, but methane had a content of 1.5 mol % nitrogen as an impurity.

Methane-Toluene. This mixture was selected to show how suitable the apparatus is to work in the critical region. Results at $T = 313.2$ K are reported in Table III and represented on Figure 2. The critical region is very well-defined; our data points are not scattered even close to the critical point ($P_c = (427 \pm 2) \times 10^5$ Pa). Savvina and Velikovskii's (3-5) results at 313.15 and 353.15 K along with those of Elbishlawi and Spencer (9) at 338.75 K are shown in Figure 2. The best agreement is between our results and those of Savvina and Velikovskii, but there is an inconsistency in the variation of critical pressure vs. temperature between the two literature data

Table III. Vapor-Liquid Equilibrium Data for the System Methane (1)-Toluene (2) at $T = 313.2$ K

$10^{-5}P$, Pa	x_1	y_1	K_1	K_2
101.0	0.237	0.991	4.18	0.012
101.0	0.234		4.24	
152.1	0.316	0.991 ^a	3.14	0.013
152.1	0.321		3.09	
196.4	0.383	0.990	2.58	0.016
250.3	0.447	0.983 ^a	2.20	0.031
300.1	0.524	0.971	1.85	0.061
300.1	0.520		1.87	0.060
349.2	0.592	0.954	1.61	0.113
380.0		0.919		
387.5	0.653	0.911	1.40	0.26
387.5	0.652			
399.5		0.894		
405.9		0.875		
408.0	0.679			
409.3		0.864		
414.9	0.701	0.837	1.19	0.55
416.9		0.835		
420.1	0.725	0.818	1.13	0.66
420.1		0.822		0.65
424.2	0.733	0.789	1.08	0.80
424.5	0.744	0.784	1.05	0.84

^a Interpolated values.

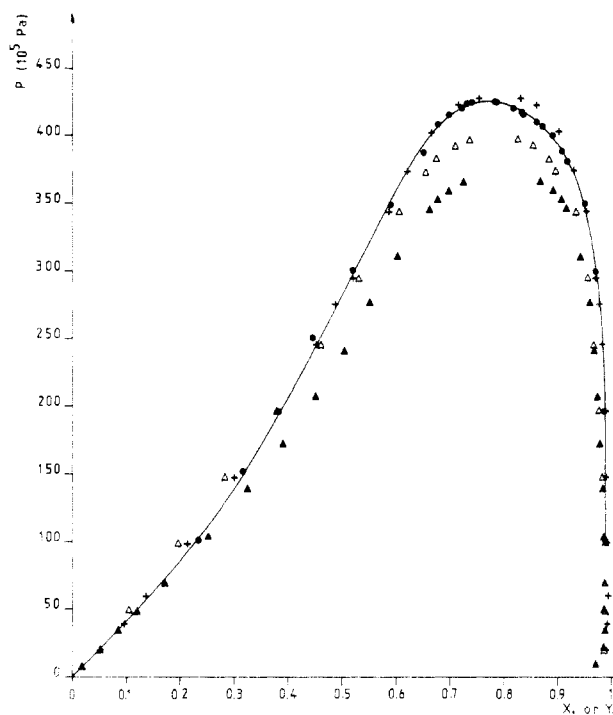


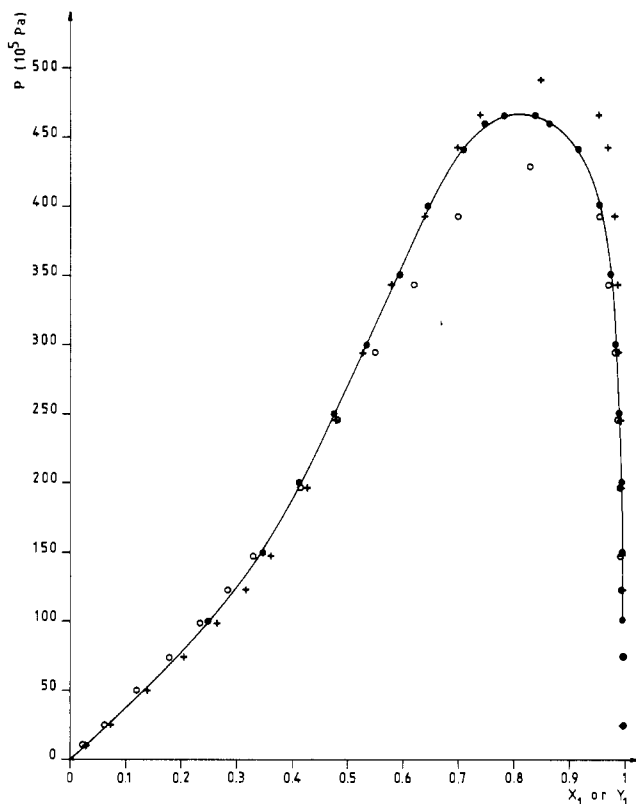
Figure 2. Vapor-liquid equilibrium data for the system methane (1)-toluene (2): (●) 313.2 K isotherm (present work), (+) 313.15 K isotherm (ref 3-5), (Δ) 353.15 K isotherm (ref 3-5), (▲) 338.75 K isotherm (ref 9).

sets; probably, the measurements of Elbishlawi and Spencer are erroneous.

Methane-m-Xylene. This mixture has been studied by Stepanova et al. (10) at 293.15 and 333.15 K and more recently by Simnick et al. (11) at 460.75, 501.55, 541.85, and 582.35 K. A new isotherm at 315.2 K was obtained in this work; the results are reported in Table IV and represented in Figure 3. Partition coefficients, K_i , are plotted vs. pressures at three temperatures in Figure 4. The three isotherms are consistent even for the *m*-xylene partition coefficient, the accuracy of its mole fraction being the worst. At 313.2 K, the critical pressure is $(467 \pm 2) \times 10^5$ Pa.

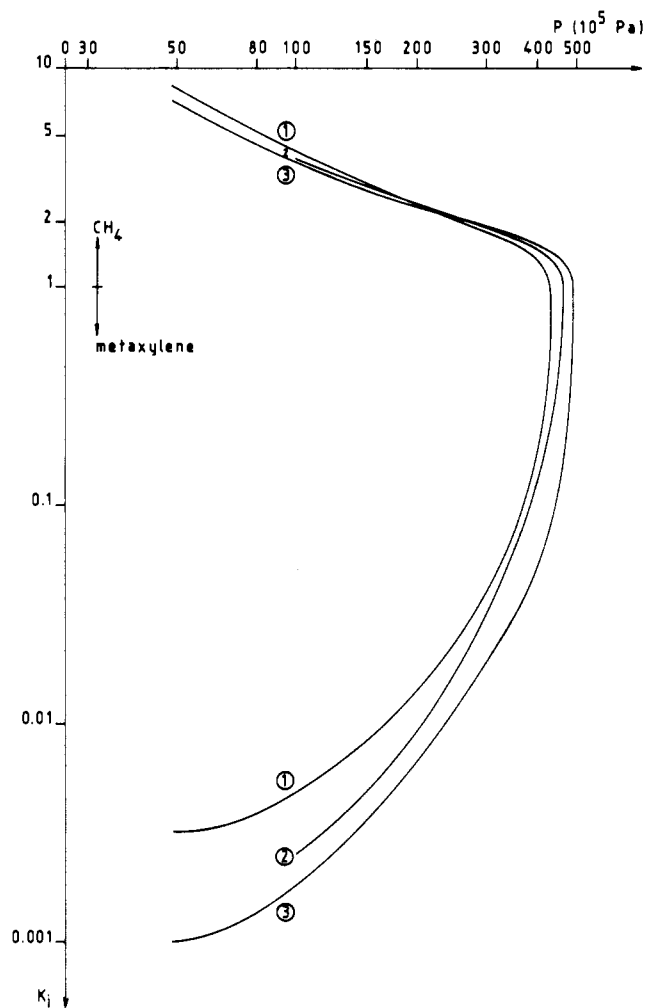
Table IV. Vapor-Liquid Equilibrium Data for the System Methane (1)-*m*-Xylene (2) at $T = 313.2$ K

$10^{-5}P$, Pa	x_1	y_1	K_1	K_2
50.6		0.998		
100.3	0.246	0.998	4.06	0.0027
	0.253		3.94	
150.1	0.345	0.997	2.89	0.0046
	0.350		2.85	
	0.348		2.86	
199.8	0.413	0.995	2.41	0.0085
250.3	0.475	0.990	2.08	0.019
	0.477			
299.3	0.535	0.983	1.84	0.037
349.8	0.595	0.975	1.64	0.062
400.6	0.645	0.956	1.48	0.124
440.3	0.710	0.919	1.29	0.279
441	0.712			0.281
459.3	0.745	0.870	1.17	0.51
459.6	0.749	0.862	1.15	0.55
465.2	0.783	0.840	1.07	0.74

Figure 3. Vapor-liquid equilibrium data for the system methane (1)-*m*-xylene (2): (●) 313.2 K isotherm (present work), (+) 293.15 K isotherm (ref 10), (O) 333.15 K isotherm (ref 10).

Methane-Mesitylene. This system does not seem to have been studied up to now. Our results are reported in Table V. The isotherm $T = 313.2$ K is represented in Figure 5 with a critical point situated at $P = (522 \pm 2) \times 10^5$ Pa.

Figure 6, where the 313.2 K isotherms of the four studied systems are plotted, shows that within a narrow P - x area the order of all solubilities is inverted. Below 320×10^5 Pa, methane solubilities increase with increasing carbon atom number while, above 370×10^5 Pa, methane solubilities decrease with increasing carbon atom number. At the same temperature, $T = 313$ K, a similar behavior is found with the systems methane-*n*-alkane (see Figure 7). The solubility inversion region is about 20×10^5 Pa centered at 100×10^5 Pa, taking into account the noted too-low solubilities reported by Stepanova et al. and the too-high one by Savvina. Our K_i partition coefficients are plotted vs. pressures in Figure 8 for

Figure 4. Partition coefficient for the system methane (1)-*m*-xylene (2): (1) 333.15 K isotherm (ref 10), (2) 313.2 K isotherm (present work), (3) 293.15 K isotherm (ref 10).Table V. Vapor-Liquid Equilibrium Data for the System Methane (1)-Mesitylene (2) at $T = 313.2$ K

$10^{-5}P$, Pa	x_1	y_1	K_1	K_2
101.7	0.278	0.9995	3.60	0.00069
	0.280		3.57	
144.5	0.355	0.9993	2.81	0.00109
	0.361		2.77	
199.5	0.428	0.998	2.33	0.0035
	0.434		2.30	
249.6	0.495	0.995	2.01	0.0099
	0.501		1.99	0.0100
298.4		0.989		
299.1	0.540	0.992	1.84	0.0174
350.2	0.589	0.984	1.67	0.039
399.3	0.649			
399.7	0.650	0.973	1.50	0.077
449.8	0.704	0.958	1.36	0.142
500.7		0.919		
501.1	0.776	0.922	1.19	0.35
510.4		0.901		
510.8	0.784	0.903	1.15	0.449
518.7		0.858		
519.1	0.808	0.860	1.06	0.729

the studied mixtures; the four curves exhibit a very consistent behavior.

Glossary

K_i	equilibrium partition coefficient for component i ($K_i = y_i/x_i$)
P	total pressure (Pa)

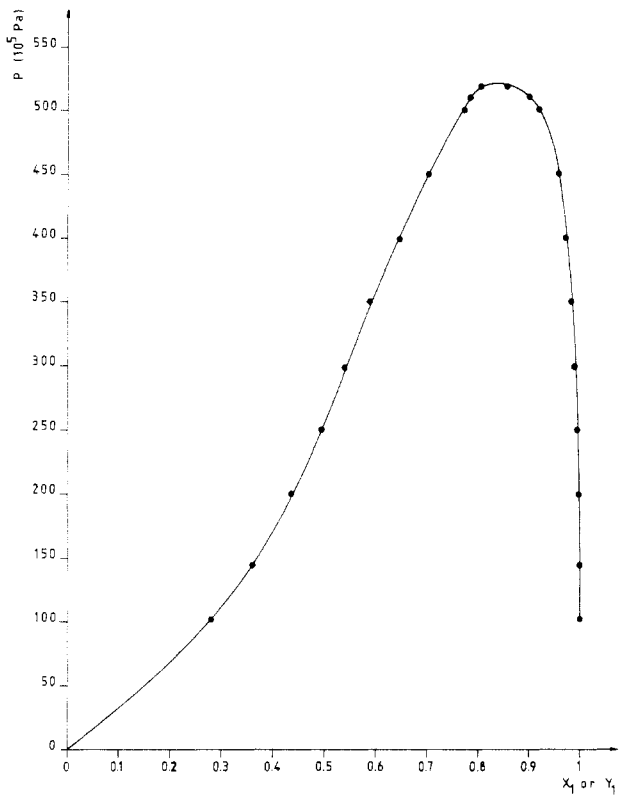


Figure 5. Vapor-liquid equilibrium data for the system methane (1)-mesitylene (2) at 313.2 K.

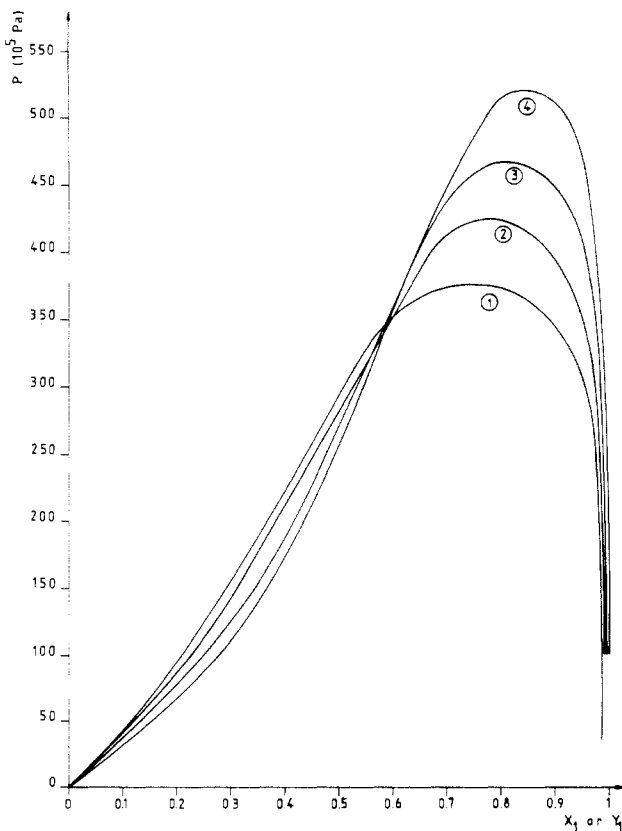


Figure 6. Vapor-liquid equilibrium data for the systems methane (1)-aromatic hydrocarbon (2) at 313.2 K: (1) methane-benzene, (2) methane-toluene, (3) methane-*m*-xylene, (4) methane-mesitylene.

T temperature (K)
 x_i liquid mole fraction of component i
 y_i vapor mole fraction of component i

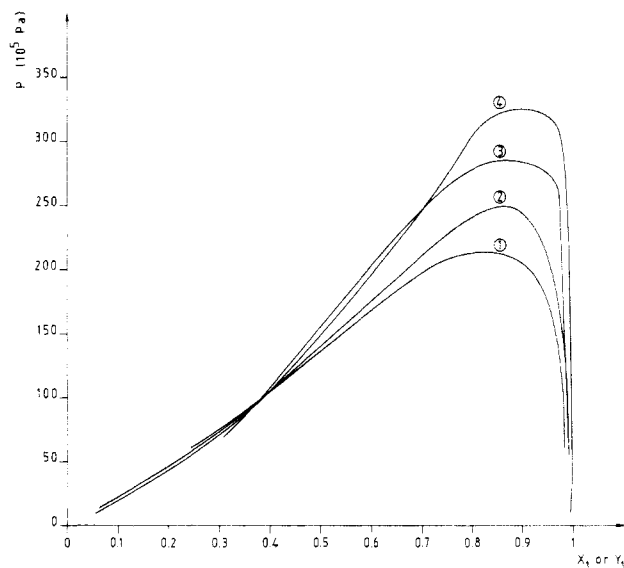


Figure 7. Vapor-liquid equilibrium data for the systems methane (1)-*n*-alkane (2): (1) methane-*n*-hexane at 313.15 K (ref 12), (2) methane-*n*-heptane at 310.95 K (ref 13), (3) methane-*n*-octane at 313.15 K (ref 14), (4) methane-*n*-nonane at 313.15 K (ref 3-5).

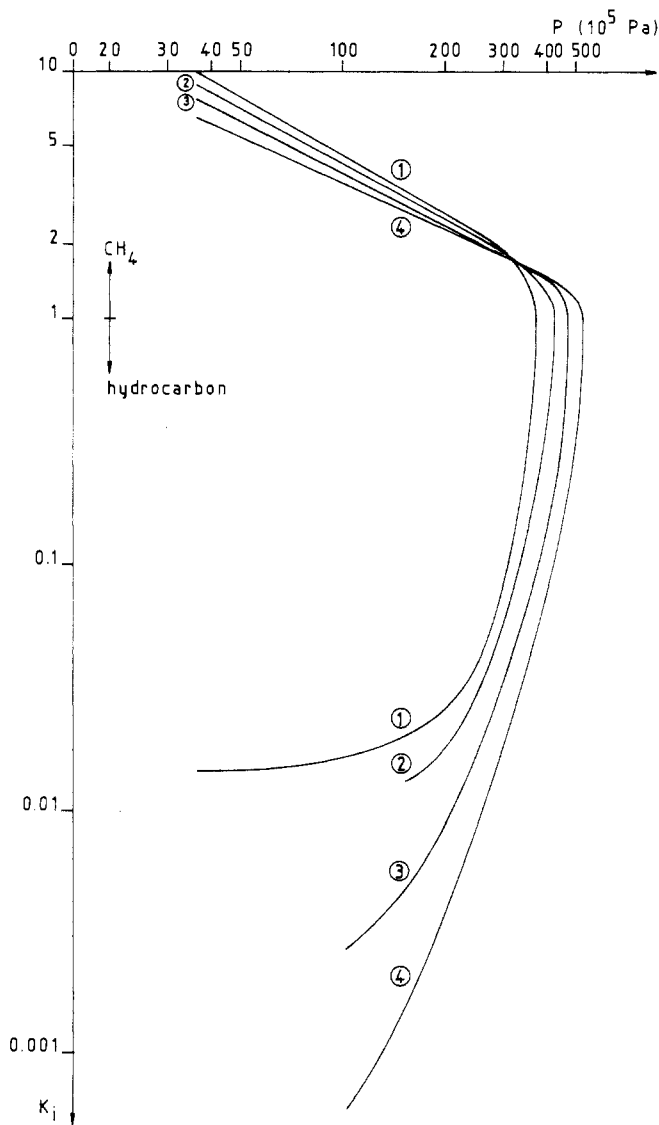


Figure 8. Partition coefficient for the systems methane (1)-aromatic hydrocarbon (2) at 313.2 K: (1) methane-benzene, (2) methane-toluene, (3) methane-*m*-xylene, (4) methane-mesitylene.

Subscripts

- 1 methane
2 hydrocarbon

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Isopiestic Determination of the Osmotic and Activity Coefficients of Aqueous CsCl, SrCl₂, and Mixtures of NaCl and CsCl at 25 °C

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The osmotic coefficients of aqueous CsCl, SrCl₂, and mixtures of NaCl and CsCl have been measured at 25 °C by the isopiestic method. The solubilities of CsCl and SrCl₂·6H₂O have also been measured at this temperature. These experimental data are compared with other available activity and solubility data and are in good agreement in most cases. Least-squares equations were used to represent the single-salt osmotic coefficients, and these equations were used to calculate water activities and mean molal activity coefficients. Data for the NaCl-CsCl solutions are accurately represented by the two-parameter form of Pitzer's equations.

Introduction

The osmotic coefficients of aqueous solutions of CsCl and SrCl₂ at 25 °C have been measured numerous times (1-12). The reported CsCl measurements exhibit systematic differences of up to 1%, while those for SrCl₂ vary up to 2%. These differences exceed by several times the expected errors for isopiestic measurements. Likewise, results for the two previous NaCl-CsCl mixed-salt isopiestic studies differ by 0.5% (2, 4). While the major errors appear to be due to low-purity chemicals used in some of the earlier studies (1, 9), additional measurements would help to clarify the situation.

Both ⁹⁰Sr and ¹³⁷Cs have the potential of becoming major biological hazards. Thermodynamic data for their chloride salts and mixtures with NaCl may help to understand their transport in the natural environment. Diffusion data for the individual salts in water have also been reported (13, 14).

In this paper isopiestic data are reported for CsCl, SrCl₂, and NaCl-CsCl mixtures. Data for NaCl-SrCl₂ mixtures will be given elsewhere (15). Isopiestic data for some of these systems at higher temperatures are being measured at Oak Ridge National Laboratory (16).

Experimental Section

Isopiestic measurements were performed at 25.00 ± 0.005 °C by using the chambers described elsewhere (17). Tables I and II contain the isopiestic equilibrium molalities (total molalities for the mixed salts) and the osmotic coefficients of the NaCl and CaCl₂ reference solutions (18, 19). These reported molalities are the average of triplicate samples for CaCl₂ and

Table I. Isopiestic Molalities of CsCl, SrCl₂, and CaCl₂ Solutions at 25 °C

[CsCl], <i>m</i>	[SrCl ₂], <i>m</i>	[CaCl ₂], <i>m</i>	φ, CaCl ₂
11.382 ^a		3.7438	2.0749
11.034		3.6734	2.0457
10.829		3.6305	2.0279
10.751	3.8426	3.6136	2.0209
10.607		3.5843	2.0088
10.579	3.8012	3.5785	2.0064
10.429		3.5480	1.9937
10.398	3.7577	3.5408	1.9907
10.372		3.5376	1.9894
10.268		3.5140	1.9796
10.043		3.4645	1.9591
9.8162		3.4163	1.9391
9.6485		3.3787	1.9236
9.4810	3.5306	3.3402	1.9076
9.4445		3.3316	1.9041
9.4359	3.5231	3.3308	1.9038
9.4242	3.5195 ^b	3.3280	1.9026
9.2848	3.4855	3.2971	1.8898
9.1402	3.4459	3.2614	1.8751
8.9903	3.4096	3.2280	1.8613
8.8705	3.3780	3.1999	1.8497
8.6588	3.3224	3.1504	1.8294
8.5441	3.2921	3.1225	1.8179
8.4055	3.2545	3.0887	1.8041
8.2792	3.2235	3.0604	1.7925
8.1648	3.1909	3.0310	1.7804
8.0337	3.1545	2.9969	1.7665
7.9146	3.1238	2.9689	1.7551
7.8034	3.0935	2.9405	1.7435
7.6963	3.0653	2.9154	1.7333
7.6898	3.0637	2.9125	1.7321
7.5528	3.0265	2.8783	1.7183
7.4328	2.9904	2.8464	1.7053
7.3307	2.9636	2.8204	1.6948
7.1658	2.9138	2.7772	1.6774
6.9960	2.8666	2.7330	1.6596
6.8196	2.8155	2.6848	1.6403
6.6493	2.7659	2.6380	1.6216
6.4850	2.7188	2.5939	1.6041
	2.6789	2.5589	1.5902

^a Saturated solution in equilibrium with solid CsCl. ^b Saturated solution in equilibrium with SrCl₂·6H₂O.

duplicate samples for the other electrolytes. Each isopiestic concentration is known to better than ±0.1%. Molecular