386 *J. Chem. Eng. Data* **1981**, *26*, 386-388

Activity Coefficients at Infinite Dilution. Paraffins, Olefins, Naphthenes, Aromatics, and Chlorides in Phenol

Yonghui Liu, Robert A. Greenkorn, and Kwang-Chu Chao*

School of Chemical Engineering, Purdue University, West Lafayette, Indiana 47907

Values of activity coefficient at infinite dilution in phenol are determined for paraffins, olefins, naphthenes, aromatics, and chlorides at 55–100 °C by the retention-time method in a specially built gas chromatograph.

Introduction

Infinite-dilution activity coefficients of solutes in pure solvents are of much interest in solution thermodynamics for the reason that they are sensitively reflective of the nonideal solution behavior of the solutes in the solvents. It has been shown (*1*) that they can be usefully applied for the calculation of real solution behavior over the complete composition range. They are also directly useful as a quantitative basis for the selection of solvents in extraction and extractive distillation.

In this work we determine the infinite-dilution activity coefficients in phenol for *n*-hexane, *n*-heptane, *n*-octane, 1-hexene, 1-heptene, 1-octene, cyclohexane, cycloheptane, methylcyclopentane, methylcyclohexane, ethylcyclohexane, cyclohexene, benzene, toluene, *p*-xylene, carbon tetrachloride, 1-chlorobutane, 1,2-dichloroethane, and 1,2-dichloropropane. Measurements were made at temperatures from 55 to 100 °C. Only a few literature data are available for these systems. Santacesaria and co-workers reported experimental results for hexane, methylcyclopentane, and cyclohexane in phenol at 45–90 °C and for benzene and toluene in phenol at 55 °C (*2*).

Apparatus and Procedure

The gas–liquid partition chromatograph and the experimental procedure that we used in this work have been described in ref *3* and *4*, where a detailed discussion of the accuracy of the results was presented, and a comparison with accepted literature data was made. The purities of chemicals which we used in this work are listed in Table I. With gaseous (argon) samples of less than 0.2 mL and liquid samples of less than 0.5 μL, retention time was determined as the elapsed time required by the injected solute to be carried by helium through the chromatograph column in which the packing was loaded with the solvent. Conductivity cells both in front of and behind the chromatograph column detect the solute vapor in the helium gas. The times of the conductivity cell output were recorded by an electronic timer as a digital signal accurate to 0.1 s.

The column temperature is controlled to within ±0.2 °C, the pressure to ±0.01 atm, and the flow rate to 1%. Reproducibility of the results has been checked with duplicate runs in some of which different amounts of solvents on the columns were used. The root mean square deviation of the duplicates never exceeded 1%. The uncertainty of the measured γ^∞ values is estimated to be below 2%.

Experimental Results

Table I. Sources and Purities of Chemicals

chemical	company	purity, %
phenol	Aldrich	99+
n-hexane	Phillips	99.99
n-heptane	Phillips	99.98
n-octane	Phillips	99.92
1-hexene	Phillips	99.98
1-heptene	Aldrich	99+
1-octene	Phillips	99.74
cyclohexane	Phillips	99.98
cycloheptane	Aldrich	99
methylcyclopentane	Aldrich	98
methylcyclohexane	Aldrich	99
ethylcyclohexane	Aldrich	99+ (bp range, 130–132 °C)
cyclohexene	Aldrich	99
benzene	Aldrich	99+
toluene	Aldrich	99+
p-xylene	Aldrich	99
carbon tetrachloride	Aldrich	99+
1-chlorobutane	Aldrich	97 (bp range, 77–78 °C)
1,2-dichloroethane	Aldrich	99+
1,2-dichloropropane	Aldrich	(bp range, 95–96 °C)

Table II. Infinite-Dilution Activity Coefficients of Paraffins and Olefins in Phenol

	p^0, atm	ϕ^0	Poynting term	$\gamma^{\infty a}$	no. of duplicates	δ, %
			55 °C			
n-hexane	0.636	0.965	1.012	14.37	5	0.4
n-heptane	0.228	0.981	1.015	17.08	4	0.9
n-octane	0.083	0.990	1.018	19.99	4	0.9
1-hexene	0.758	0.962	1.011	9.24	4	1.0
1-heptene	0.271	0.979	1.015	10.52	4	0.9
1-octene	0.099	0.989	1.017	12.23	4	1.0
			70 °C			
n-hexane	1.040	0.951	1.010	12.85	5	0.7
n-heptane	0.400	0.973	1.014	14.83	5	0.7
n-octane	0.157	0.985	1.017	16.97	4	0.5
1-hexene	1.224	0.948	1.008	8.30	4	0.5
1-heptene	0.469	0.970	1.013	9.46	4	0.9
1-octene	0.184	0.984	1.016	10.65	4	1.0
			85 °C			
n-hexane	1.622	0.935	1.010	12.10	5	0.8
n-heptane	0.663	0.962	1.016	13.47	3	0.5
n-octane	0.277	0.978	1.020	15.10	3	0.5
1-hexene	1.887	0.931	1.008	7.86	4	0.9
1-heptene	0.769	0.958	1.015	8.75	3	0.7
1-octene	0.321	0.976	1.019	9.77	3	0.7
			100 °C			
n-hexane	2.421	0.917	1.009	11.70	6	0.8
n-heptane	1.047	0.949	1.017	12.81	3	0.6
n-octane	0.462	0.969	1.022	14.15	3	0.6
1-hexene	2.828	0.911	1.006	7.71	3	0.5
1-heptene	1.202	0.944	1.016	8.39	3	0.8
1-octene	0.530	0.967	1.021	9.33	3	0.7

[a] Average of duplicates.

Activity coefficients were derived from the experimental retention-time data for all of the systems studied in this work according to eq 1. The equation has been discussed (*3–5*),

$$\gamma_i^\infty = \frac{p\phi_i K_i}{p_i^0 \phi_i^0 \exp[(p - p_i^0)\tilde{V}_{il}/RT]} \qquad (1)$$

and the symbols are explained in the Glossary. The saturated-vapor fugacity coefficient ϕ_i^0 was taken from the generalized correlation by Lyderson et al. (*6*). Vapor pressure p_i^0 was

0021-9568/81/1726-0386$01.25/0

Table III. Infinite-Dilution Activity Coefficients of Naphthenes in Phenol

	p^0, atm	ϕ^0	Poynting term	$\gamma^{\infty a}$	no. of duplicates	δ, %
		55 °C				
cyclohexane	0.430	0.978	1.010	8.48	5	0.4
cycloheptane	0.116	0.990	1.013	8.85	4	0.5
methylcyclopentane	0.578	0.971	1.010	9.36	4	0.6
methylcyclohexane	0.221	0.984	1.013	10.57	3	0.2
ethylcyclohexane	0.074	0.992	1.016	12.28	3	1.0
cyclohexene	0.397	0.979	1.010	5.25	3	0.5
		70 °C				
cyclohexane	0.716	0.969	1.009	7.59	4	0.5
cycloheptane	0.210	0.985	1.012	7.89	3	1.0
methylcyclopentane	0.945	0.961	1.008	8.27	3	0.6
methylcyclohexane	0.381	0.977	1.012	9.44	3	0.2
ethylcyclohexane	0.137	0.988	1.015	10.65	3	0.9
cyclohexene	0.666	0.971	1.009	4.76	3	0.4
		85 °C				
cyclohexane	1.135	0.958	1.010	7.10	4	0.5
cycloheptane	0.359	0.979	1.014	7.42	3	0.7
methylcyclopentane	1.475	0.947	1.009	7.70	3	0.4
methylcyclohexane	0.623	0.969	1.014	8.65	3	0.2
ethylcyclohexane	0.239	0.982	1.018	9.79	4	1.0
cyclohexene	1.063	0.961	1.010	4.60	3	0.6
		100 °C				
cyclohexane	1.724	0.945	1.010	6.97	4	0.6
cycloheptane	0.581	0.971	1.016	7.28	3	0.8
methylcyclopentane	2.209	0.932	1.008	7.64	3	0.5
methylcyclohexane	0.973	0.958	1.015	8.45	4	0.4
ethylcyclohexane	0.396	0.975	1.019	9.04	3	0.9
cyclohexene	1.624	0.948	1.009	4.47	3	0.6

[a] Average of duplicates.

Table IV. Infinite-Dilution Activity Coefficients of Aromatics in Phenol

	p^0, atm	ϕ^0	Poynting term	$\gamma^{\infty a}$	no. of duplicates	δ, %
		55 °C				
benzene	0.430	0.980	1.009	2.87	4	0.3
toluene	0.149	0.989	1.011	3.45	4	0.5
		70 °C				
benzene	0.725	0.972	1.007	2.62	4	0.4
toluene	0.268	0.984	1.011	3.00	4	0.4
p-xylene	0.104	0.990	1.014	3.49	2	0.7
		85 °C				
benzene	1.160	0.962	1.008	2.53	4	0.6
toluene	0.454	0.977	1.012	2.89	4	0.9
p-xylene	0.186	0.986	1.016	3.26	2	0.9
		100 °C				
benzene	1.777	0.950	1.008	2.49	4	1.0
toluene	0.732	0.969	1.013	2.84	4	0.6
p-xylene	0.316	0.980	1.017	3.22	2	0.9

[a] Average of duplicates.

Table V. Infinite-Dilution Activity Coefficients of Chlorides in Phenol

	p^0, atm	ϕ^0	Poynting term	$\gamma^{\infty a}$	no. of duplicates	δ, %
		55 °C				
carbon tetrachloride	0.491	0.977	1.009	4.56	3	0.5
1-chlorobutane	0.456	0.971	1.010	3.68	3	0.6
1,2-dichloroethane	0.372	0.980	1.008	2.41	4	0.8
1,2-dichloropropane	0.244	0.983	1.010	2.81	4	0.6
		70 °C				
carbon tetrachloride	0.811	0.968	1.008	4.19	3	0.7
1-chlorobutane	0.765	0.960	1.009	3.34	5	0.7
1,2-dichloroethane	0.638	0.972	1.007	2.14	3	0.6
1,2-dichloropropane	0.426	0.976	1.009	2.48	3	0.5
		85 °C				
carbon tetrachloride	1.278	0.958	1.008	4.08	3	1.1
1-chlorobutane	1.219	0.947	1.009	3.25	4	0.8
1,2-dichloroethane	1.038	0.962	1.008	2.03	4	0.4
1,2-dichloropropane	0.705	0.967	1.011	2.35	4	0.5
		100 °C				
carbon tetrachloride	1.930	0.945	1.008	3.89	3	0.9
1-chlorobutane	1.861	0.931	1.009	3.18	3	1.1
1,2-dichloroethane	1.626	0.949	1.007	2.03	3	1.0
1,2-dichloropropane	1.111	0.956	1.011	2.36	3	1.1

[a] Average of duplicates.

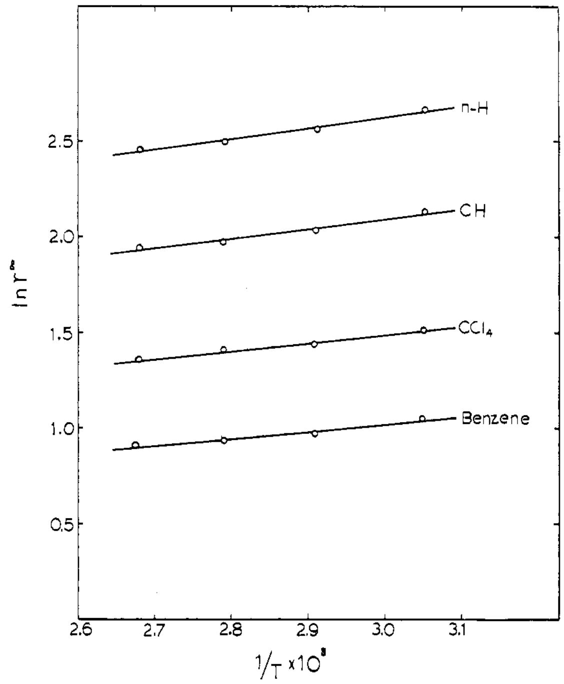

Figure 1. Infinite-dilution activity coefficients of some solutes in phenol.

taken from American Petroleum Institute Research Project 44 Tables (*7*) and Harlarcher's compilation (*8*). The *K* values of solutes in eq 1 were obtained from the experimentally observed variables according to

$$K_i = \frac{nz_aRT_a}{p_aF_a(t_{Ri} - t_g)} \qquad (2)$$

The weight of solvent on the chromatograph column changed up to 4% during the course of a series of experiments. Therefore, the amount of solvent was determined by weighing both at the beginning and at the end. The retention time of *n*-hexane was determined at regular intervals in between and was used to interpolate for the amount of solvent for an experiment.

Tables II–V show γ^∞ values obtained in this work. The tabulated data are average values of duplicate runs. The number of duplicates and their root mean square relative deviations are reported. The latter is found to be within 1% for all of the experiments.

Figure 1 shows plots of log γ^∞ vs. $1/T$ for *n*-hexane, cyclohexane, carbon tetrachloride, and benzene. The results are linear. Similar linear results are obtained for the other solutes but are not shown to avoid repetition.

Santacesaria et al. (*2*) reported γ^∞ values for *n*-hexane and cyclohexane in phenol. Figure 2 shows that their results coincide with ours at ~60 °C but diverge at other temperatures with the largest deviations amounting to ~10%, which appears

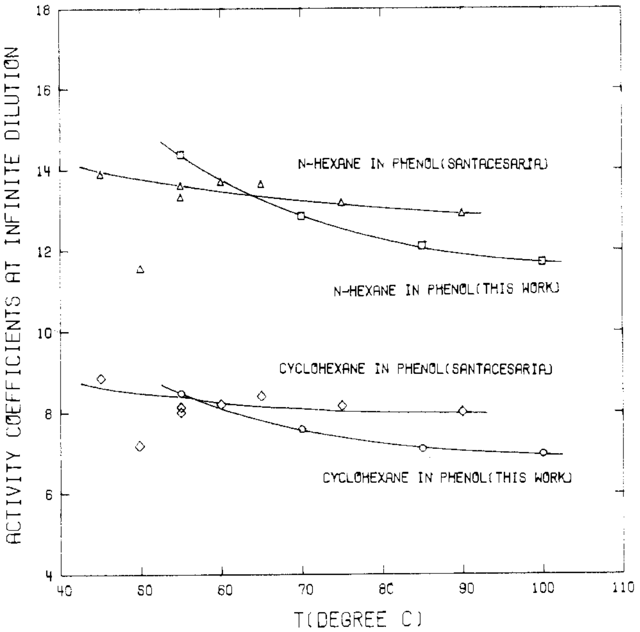

Figure 2. Comparison of γ^{∞} values obtained in this work and reported by Santacesaria (*2*).

to be within the uncertainty of their data. There is as much deviation between their own data from the chromatograph method and from a transient desorption method.

Glossary

F_a	volumetric flow rate of elution gas at ambient conditions
K_i	equilibrium y_i/x_i for component i
n	moles of stationary liquid phase on column packing
p	column pressure
p_a	ambient pressure
p^0	vapor pressure
R	gas constant
t_{Ri}	retention time of solute i
t_g	retention time of hypothetical "nonabsorbed" gas
T	absolute temperature
T_a	absolute ambient temperature
$\bar{V}_{li}$	liquid molar volume of component i
z_a	compressibility factor of elution gas at ambient conditions
δ	root mean square relative deviation of the duplicates from their average γ value
γ^{∞}_i	activity coefficient of component i in the liquid phase at T
ϕ_i	fugacity coefficient of component i in the elution gas at T and p
ϕ_i^0	fugacity coefficient of pure vapor i and T and p_i^0

Literature Cited

(1) Schreiber, L. B.; Eckert, C. A. *Ind. Eng. Chem., Process Des. Dev.* **1971**, *10*, 572.
(2) Santacesaria, E.; Berlendis, D.; Carra, S. *Fluid Phase Equilib.* **1979**, *3*, 167.
(3) Turek, E. A.; Comanita, J; Greenkorn, R. A.; Chao, K. C. *J. Chem. Eng. Data* **1976**, *21*, 209.
(4) Turek, E. A.; Arnold, D. W.; Greenkorn, R. A.; Chao, K. C. *Ind. Eng. Chem. Fundam.* **1979**, *18*, 426.
(5) Yudovich, A.; Robinson, R. L.; Chao, K. C. *AIChE J.* **1963**, *9*, 121.
(6) Lyderson, A. L.; Greenkorn, R. A.; Hougen, O. A. "Generalized Thermodynamic Properties of Pure Fluids", Engineering Experiment Station Report No. 4; University of Wisconsin: Madison, WI, 1955.
(7) American Petroleum Institute, Research Project 44. "Selected Values of Properties of Hydrocarbons and Related Compounds", 1954.
(8) Harlarcher, E. A.; Braun, W. G. *Ind. Eng. Chem., Process Des. Dev.* **1970**, *9*, 479.

Received for review November 10, 1980. Accepted May 12, 1981. Financial support for this work was partly derived from National Science Foundation Grant CPE-7912455.

Solubility of Carbon Dioxide in Liquid Water and of Water in Gaseous Carbon Dioxide in the Range 0.2–5 MPa and at Temperatures up to 473 K

Andrzej Zawisza* and Bogusława Malesińska
Institute of Physical Chemistry of the Polish Academy of Sciences, 01-224 Warsaw, Poland

Boiling points and dew-point pressures, as well as the isotherms p–V between dew points and the pressures of 0.2 MPa of the water + carbon dioxide system, have been determined for temperatures up to 473 K. The Henry constants were calculated for the range of temperatures 323–473 K.

Introduction

The system water + carbon dioxide has caught the attention of many investigators because of technological and geothermal aspects. There are many papers concerning the liquid-vapor and gas-gas equilibria in various ranges below 350 MPa and between 298 and 623 K (*1–8*).

The system water + carbon dioxide belongs to type III of the classification introduced by Scott and van Konynenburg (*9*). The critical-temperature curve of the carbon dioxide rich phase starts at the critical temperature of pure carbon dioxide and comes to the upper critical end point. The critical-temperature curve of the water-rich phase starts with the critical temperature of pure water and reaches the area of limited solubility of gases near 539 K and 200 MPa.

This work was undertaken because of the lack of data in the range of 373–473 K below 10 MPa. The data of Takenouchi and Kennedy (*6*) and Todheide and Franck (*5*) start at 10 or 20 MPa, while those of Wiebe and Gaddy (*1–3*) cover the range of temperatures 285–373 K.

Experimental Section

Materials. Carbon dioxide was prepared by treatment of sodium carbonate with a 10% aqueous solution of sulfuric acid dried with phosphorus pentoxide and liquefied in a stainless-steel

0021-9568/81/1726-0388$01.25/0