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Infinite-Dilution Activity Coefficients of Organic Solutes in Fluorene and Dibenzofuran

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Infinite-dilution activity coefficients are determined in a gas–liquid partition chromatograph for 10 solutes in the stationary phases fluorene and dibenzofuran. The column temperatures are from 90 to 160 °C with column operating pressures up to 2.71 atm. The experimental activity coefficients are correlated with the Soave and the Peng–Robinson equations of state.

Introduction

Activity coefficients are a fundamental thermodynamic property of liquid mixtures. They provide a measure of the deviation from ideality of a component's behavior in a mixture. Activity coefficients at infinite dilution (γ^∞) are important because solution effects are often greatest at infinite dilution. Gas–liquid partition chromatography is a rapid method for determination of γ^∞ and has been extensively studied (*1*, *2*).

Data are reported in this work for 10 solutes in the stationary phases fluorene and dibenzofuran in the temperature range from 90 to 160 °C with column pressures from 1.34 to 2.71 atm. The solutes are alkanes, arenes, and alkanones. Additionally the stationary phase *n*-hexadecane is studied for comparison with literature values.

Experimental Section

Figure 1 shows the modified Varian Aerograph Series 2700 gas chromatograph used to make the experimental measurements. The pressure within the chromatograph was controlled by a Matheson two-stage pressure tank regulator and a gas-flow controller on the chromatograph. The outlet pressure for the reference side was atmospheric; the packed-column-side outlet pressure was controlled by a Whitey Model SS-22RS2 fine metering valve with a Viton O-ring. The inlet and outlet pressures of the packed column were measured with a Heiss pressure gauge. Positive shut-off toggle valves facilitated switching from the inlet to outlet side. Temperatures were measured with type-J thermocouples and displayed by a Doric Series 400A digital temperature readout. The thermocouples were calibrated with a platinum resistance thermometer, and the pressure gauge was calibrated with a dead-weight tester. The calibration procedures are described in detail elsewhere (*3*). The flow rate was measured with a soap bubble flowmeter and stopwatch. A Hewlett-Packard Model 3990A reporting integrator provided the retention time to 0.001 min and a peak area that is a function of the amount of solute injected. It is this peak area that is used to calculate the reduced sample size. The chromatograph was equipped with a thermal conductivity cell as a detector. After the gas passes through the cell, the packed-column-side gas passes through a cold trap where all volatile material is condensed and removed before the gas is passed through the soap bubble flowmeter. The temperature control was modified by adding a 50-ohm variable resistor in series with the existing oven control to allow column temperature regulation to within ±0.1 °C. Two small brass canisters were placed in the packed-column side, one as a bubbler to presaturate the gas stream with solvent and the other to prevent any possible kickback of liquid in the system. The areas where the solvent-laden gas stream traveled outside the oven were wrapped in heating tape and insulated to prevent plugging by fluorene or dibenzofuran. In an effort to diminish dead-volume effects all tubing after the injector and to the detector was 1/16-in. stainless steel. Leak tests were done periodically to ensure all Swagelock fitting connections were tight. The source and purity of the chemicals used in this study are presented in Table I. The experimental operating parameters are presented in Table II. Purification methods and analytical procedures are given in ref *3* and *4*.

Table I. Chemicals Used in Experimental Work

compound	source	% purity
n-hexane	Aldrich	99+
n-heptane	Aldrich	99+
n-octane	Aldrich	99+
n-nonane	Aldrich	99
cyclohexane	MCB	99.1
benzene	Aldrich	99+
toluene	Aldrich	99+
p-xylene	Aldrich	99+
2-butanone	Aldrich	99.9
3-pentanone	Aldrich	98.3
n-hexadecane	MCB	99+
fluorene	Chemalog	99+[a]
dibenzofuran	Aldrich	99+[a]
helium	Airco (purified, grade 4.5)	99.995

[a] By GC/MS.

Data Reduction

Data reduction follows the method in ref *2*. The net retention volume at the column temperature T and column outlet pressure P is given by

$$V_N(T,P) = jt_R\left[F\left(\frac{273.15}{T_R}\right)\left(\frac{P_B}{1}\right)\left(1-\frac{P^\circ_w}{760}\right)\right]\left(\frac{T}{273.15}\right)\left(\frac{1}{P}\right) \tag{1}$$

where j is the pressure-gradient correction factor, t_R is the net retention time, F is the flow rate, T_R is the room temperature, P_B is the barometric pressure, and P°_w is the vapor pressure of water at room temperature. The term in brackets is the dry carrier gas flow rate. The specific retention volume $V_g(T,P)$ at the column temperature and pressure is

$$V_g(T,P) = V_N(T,P)/W_L \tag{2}$$

were W_L is the mass of the stationary phase on the column. Figure 2 is a flow-rate check to ensure that $V_g(T,P)$ is independent of the flow rate.

Figures 3 and 4 are examples of the extrapolation procedure to obtain specific retention volumes, $V_g^\infty(T,P)$, at zero sample size. The maximum sample size used is 0.5 μL, and the reduced sample size is the peak area divided by the maximum

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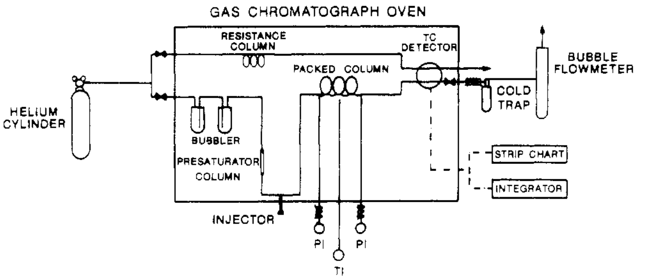

Figure 1. Schematic of gas chromatograph for measuring infinite-dilution activity coefficients.

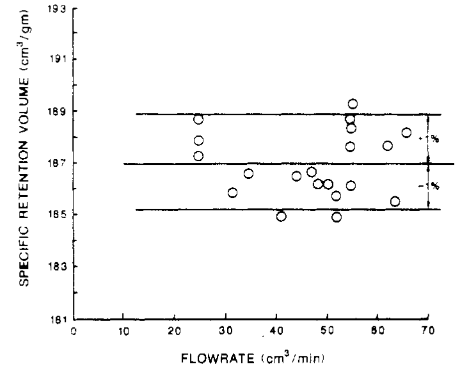

Figure 2. Specific retention volume versus flow rate for *n*-hexane in *n*-hexadecane at 60 °C (sample size 0.3–0.5 L).

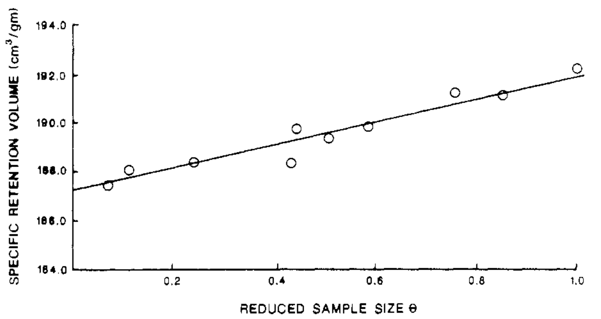

Figure 3. Specific retention volume versus reduced sample size for *n*-hexane in *n*-hexadecane at 60 °C (38.9 wt % loading).

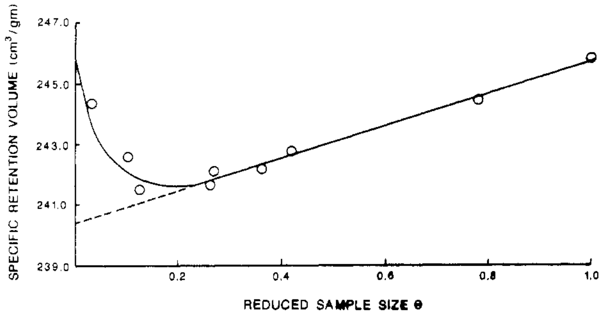

Figure 4. Specific retention volume versus reduced sample size for 3-pentanone in *n*-hexadecane at 60 °C (48.2 wt % loading).

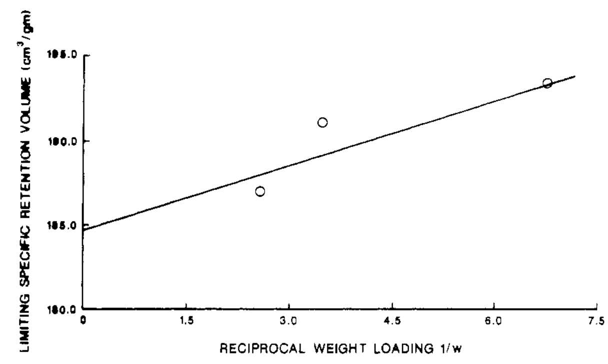

Figure 5. Limiting specific retention volume versus reciprocal weight loading for *n*-hexane in *n*-hexadecane at 60 °C.

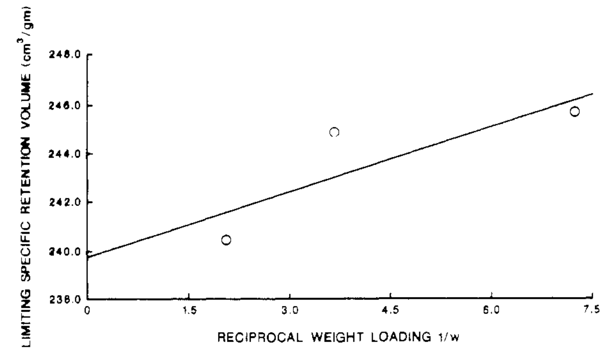

Figure 6. Limiting specific retention volume versus reciprocal weight loading for 3-pentanone in *n*-hexadecane at 60 °C.

peak area. Figures 5 and 6 are examples of the extrapolation of $V_g^\infty(T,P)$ to 100% liquid loading in the column. The weight loading W is equal to the weight of the liquid in the column divided by the weight of stationary phase in the column.

Infinite-dilution activity coefficients are calculated from the equation

$$\gamma_p^\infty = \frac{RT}{P^\circ M_L V_g^\infty(T,P)} \tag{3}$$

where R is the gas constant, P° is the vapor pressure of the solute, and M_L is the molecular weight of the stationary phase. Corrections for gas-phase imperfections are made by

$$\ln \gamma^\infty = \ln \gamma_p^\infty + \left(\frac{V-B}{RT}\right)P^\circ \tag{4}$$

where V is the molar volume of the pure liquid solute and B is the second virial coefficient of the solute.

Results

Table III is a comparison of literature values with this work. Tables IV–X contain the specific retention volumes, the corrected and uncorrected infinite-dilution activity coefficients, liquid molar volumes (cm³/mol), second virial coefficients (cm³/mol), and vapor pressures (atm). The values of V, B, and P° are from standard correlations that are given in ref *3* and *4*. The reproducibilities of the retention data in successive runs are ±1.0%. The accuracy of the activity coefficients is also affected by the extrapolation procedure. The accuracy of the activity coefficients is believed to be within ±1.8%.

The temperatures for the fused-ring aromatic stationary phases are set by being above their melting points and low enough to prevent excessive stripping of the stationary phase off the column. Stripping was limited to 4% of the initial weight on the column.

Correlation of Results

The Soave–Redlich–Kwong (SRK) (*8*) and the Peng–Robinson (PR) (*9*) equations of state (EOS) are chosen because of their wide use in VLE calculations and their simplicity. Although activity coefficients are not used directly in VLE calculations with EOS, interaction parameters from infinite-dilution equilibrium data can be used for finite concentration calculations (*10*). The method for calculating activity coefficients is the same as ref *11*. The actual system pressure is the vapor pressure of the pure stationary phase at the specified temperature. For this

Table II. Experimental Operating Parameters

column specification	1/4-in. tubing, 6–18 in. long
tubing	
constructional material	type 304 precleaned stainless steel
support	
nature and pretreatment	acid-washed, DMCS-treated diatomite
mesh range	60/80
packing	
method of coating	dissolve stationary phase in diethyl ether, vaporize, and remove ether in a stream of helium, weigh entire column[a]
% loading	
n-hexadecane	13–49
fluorene	30–45
dibenzofuran	39–40
mass of stationary phase in column	
n-hexadecane	0.96–2.2 g
fluorene	1.6–3.6 g
dibenzofuran	2.4–3.8 g
end-plug material	glass wool
method of gas holdup measurement	air peak
chromatograph and apparatus	
model	Varian Aerograph Series 2700
injection method	syringe injection through standard septum
detector type	thermal conductivity cell
recorder	Hewlett-Packard 3390-A, reporting integrator
flow control, measurement	needle valve, soap bubble flowmeter
column temp control, measurement	air bath, type-J thermocouple accurate to ±0.2 °C
experimental conditions	
vapor press. of stationary phase at column temp	
n-hexadecane	0.03 mmHg at 60 °C
	2.3 mmHg at 120 °C
fluorene	3.4 mmHg at 120 °C
	7.9 mmHg at 140 °C
	16.8 mmHg at 160 °C
dibenzofuran	2.9 mmHg at 90 °C
	6.5 mmHg at 110 °C
	12.9 mmHg at 130 °C
detector temp and current	190–200 °C, 135–175 mA
injection temp	150–185 °C
column outlet press. and press. drop	accurate to ±0.25 psia
n-hexadecane	19.7–31.7 psia, 1.0–2.5 psia
fluorene	23.0–39.9 psia, 1.0–4.0 psia
dibenzofuran	23.9–27.6 psia, 1.5–3.9 psia
flow rate of dry carrier gas	accurate to ±0.5 cm^3/min
n-hexadecane	25 to 65 cm^3/min
fluorene	19 to 63 cm^3/min
dibenzofuran	18 to 32 cm^3/min
melting point	
n-hexadecane	18 °C
fluorene	115 °C
dibenzofuran	84 °C

[a] Details are given in ref *3*.

Table III. Comparison of γ^∞ for *n*-Hexane in *n*-Hexadecane at 60 °C of This Work with Literature Values

investigator	technique	γ^∞	% diff
this work	GC	0.907	
McGlashan and Williamson (*5*)	static	0.897	1.1
Chen and Parcher (*6*)	GC	0.901	0.67
Turek, Arnold, Greenkorn, Chao (*7*)	GC	0.899	0.89

work that is only a few Torr and the EOS calculations are unstable. All calculations were done at a pressure of 1 atm. Small pressure changes in this region have little effect on the calculated activity coefficients. Infinite dilution is obtained by using small concentrations and extrapolating to 0 mole fraction. This procedure introduces little error.

In Table XI are the interaction parameters (C_{ij}) for the two fused-ring stationary phases. Figure 7 is a plot of the calculated infinite-dilution activity coefficients compared to the experimental values. The solid line represents activity coefficients from the PR EOS with C_{ij} set to zero, and the dashed line is a fit to the experimental values. As can be seen from Table XI, both equations fit the data within experimental error. The bottom row in Table XI is the percent difference between the experimental and the calculated activity coefficient with the interaction parameter set to zero. The large deviations in this last column (with $C_{ij} = 0$) are due, in large part, to the normal paraffins such as *n*-nonane. Additional details on the EOS calculations are given in ref *4*.

Table IV. Specific Retention Volumes and Activity Coefficients at Infinite Dilution in *n*-Hexadecane at 60 and 120 °C

	at 60 °C						at 120 °C		
solute	$V_g^\infty(T,P)$, cm^3/g	γ_P^∞	γ^∞	V	B	P°	$V_g^\infty(T,P)$, cm^3/g	γ_P^∞	γ^∞
n-hexane	185	0.869	0.907	157.9	−1427	0.7522	46.4	0.782	0.897
benzene	247	0.951	0.974	107.2	−1178	0.5149	61.2	0.789	0.856
3-pentanone	240	2.17	2.21	126.0	−2224	0.2324	54.2	1.56	1.68

Table V. Specific Retention Volumes and Activity Coefficients at Infinite Dilution in Fluorene at 120 °C

compound	$V_g^\infty(T,P)$	γ_p^∞	γ^∞	V	B	P°
n-hexane	18.6	2.66	3.05	207.4	-920.9	3.927
n-heptane	37.8	2.85	3.10	226.9	-1300.0	1.800
n-octane	77.1	2.96	3.12	248.1	-1787	0.8516
n-nonane	161	2.94	3.04	270.5	-2380	0.4107
cyclohexane	34.7	1.96	2.15	165.2	-860.5	2.853
benzene	56.9	1.16	1.26	137.3	-755.4	2.950
toluene	124	1.21	1.27	160.1	-1123	1.298
p-xylene	270	1.22	1.26	184.9	-1631	0.588
2-butanone	41.1	1.55	1.73	139.0	-984.9	3.04
3-pentanone	80.6	1.43	1.55	162.5	-1266	1.680

Table VI. Specific Retention Volumes and Activity Coefficients at Infinite Dilution in Fluorene at 140 °C

compound	$V_g^\infty(T,P)$	γ_p^∞	γ^∞	V	B	P°
n-hexane	13.1	2.58	3.14	284.2	-813.9	6.05
n-heptane	25.4	2.75	3.09	247.3	-1134	2.92
n-octane	47.5	2.94	3.18	269.4	-1553	1.46
n-nonane	97.2	2.80	2.95	292.5	-2048	0.749
cyclohexane	24.8	1.85	2.09	179.4	-763.0	4.46
benzene	37.8	1.16	1.30	148.9	-669.2	4.65
toluene	76.9	1.23	1.33	173.0	-984.2	2.16
p-xylene	159	1.25	1.31	199.4	-1413	1.03
2-butanone	27.2	1.56	1.79	151.5	-850.6	4.83
3-pentanone	50.3	1.44	1.60	176.5	-1090	2.82

Table VII. Specific Retention Volumes and Activity Coefficients at Infinite Dilution in Fluorene at 160 °C

compound	$V_g^\infty(T,P)$	γ_p^∞	γ^∞	V	B	P°
n-hexane	10.2	2.38	2.98	169.7	-725	8.89
n-heptane	18.8	2.52	2.94	186.2	-1003	4.53
n-octane	34.2	2.64	2.93	201.2	-1363	2.38
n-nonane	61.8	2.74	2.94	219.9	-1784	1.27
cyclohexane	19.0	1.71	2.00	133.2	-684	6.61
benzene	27.9	1.10	1.26	109.8	-598	6.99
toluene	54.7	1.16	1.28	126.6	-876	3.39
p-xylene	98.6	1.26	1.35	146.2	-1240	1.73
2-butanone	19.7	1.45	1.75	112.2	-768	7.54

Table VIII. Specific Retention Volumes and Activity Coefficients at Infinite Dilution in Dibenzofuran at 90 °C

compound	$V_g^\infty(T,P)$	γ_p^∞	γ^∞	V	B	P°
n-hexane	30.7	3.10	3.36	144.3	-1129	1.86
n-heptane	70.5	3.24	3.39	163.5	-1615	0.776
n-octane	160	3.36	3.45	179.7	-2267	0.330
n-nonane	362	3.42	3.48	198.9	-3075	0.143
cyclohexane	59.5	2.27	2.39	118.4	-1056	1.31
benzene	107.0	1.24	1.30	98.1	-926	1.34
toluene	255.0	1.30	1.34	114.4	-1412	0.535
p-xylene	602	1.32	1.34	133.3	-2089	0.223
2-butanone	92.3	1.40	1.50	97.6	-1396	1.37
3-pentanone	188.0	1.37	1.43	126.6	-1676	0.685

Table IX. Specific Retention Volumes and Activity Coefficients at Infinite Dilution in Dibenzofuran at 110 °C

compound	$V_g^\infty(T,P)$	γ_p^∞	γ^∞	V	B	P°
n-hexane	20.1	2.99	3.34	150.0	-983	3.11
n-heptane	42.8	3.14	3.36	168.9	-1389	1.39
n-octane	89.3	3.30	3.44	185.0	-1927	0.634
n-nonane	188.0	3.36	3.45	204.2	-2581	0.295
cyclohexane	37.9	2.21	2.38	122.0	-920	2.23
benzene	65.2	1.24	1.33	100.9	-806	2.31
toluene	146.0	1.30	1.36	117.5	-1211	0.982
p-xylene	314.0	1.36	1.40	136.6	-1764	0.438
2-butanone	53.6	1.46	1.61	101.1	-1151	2.39
3-pentanone	107.0	1.38	1.47	130.4	-1394	1.27

Glossary

B	second virial coefficient, cm^3/mol
C_{ij}	binary interaction parameter
F	carrier gas flow rate, cm^3/min
j	pressure-gradient correction factor

Table X. Specific Retention Volumes and Activity Coefficients at Infinite Dilution in Dibenzofuran at 130 °C

compound	$V_g^\infty(T,P)$	γ_p^∞	γ^∞	V	B	P°
n-hexane	14.4	2.78	3.23	156.8	-865	4.91
n-heptane	28.9	2.93	3.23	175.1	-1210	2.32
n-octane	57.9	3.00	3.20	190.9	-1663	1.13
n-nonane	108.0	3.27	3.41	210.0	-2204	0.557
cyclohexane	26.4	2.08	2.30	126.1	-811	3.58
benzene	43.7	1.21	1.32	104.2	-710	3.74
toluene	93.6	1.25	1.33	120.8	-1054	1.68
p-xylene	188.6	1.31	1.36	140.1	-1516	0.796
2-butanone	34.9	1.43	1.63	105.0	-968	3.93
3-pentanone	67.6	1.33	1.45	134.6	-1181	2.19

Table XI. Binary Interaction Parameters (C_{ij}) for the Peng–Robinson (PR) and Soave (RKS) Equation of States for the Stationary Phases Fluorene and Dibenzofuran[a]

	fluorene		dibenzofuran	
compound	PR	SRK	PR	SRK
n-hexane	–0.0285	–0.0348	0.0059	0.0012
n-heptane	–0.0332	–0.0395	0.0004	–0.0035
n-octane	–0.0434	–0.048	–0.0098	–0.0129
n-nonane	–0.0496	–0.0535	–0.0137	–0.0168
cyclohexane	0.0090	0.0051	0.0355	–0.0332
benzene	–0.0027	–0.0051	0.0105	0.0090
toluene	–0.0121	–0.0145	0.0035	0.0020
p-xylene	–0.0223	–0.0246	–0.0035	–0.0059
2-butanone	0.0027	–0.0004	0.0113	0.0090
3-pentanone	–0.0113	–0.0145	–0.0004	–0.0027
av abs % diff (C_{ij} given above)[b]	1.63	1.43	1.83	1.73
av abs % diff (C_{ij} = 0)[b]	63.4	73.4	14.6	15.8

[a] $A_{ij} = (A_iA_j)^{1/2}(1 - C_{ij})$. [b] Percent difference = $[(\gamma^\infty_{\text{calcd}} - \gamma^\infty_{\text{exptl}})/\gamma^\infty_{\text{exptl}}] \times 100$.

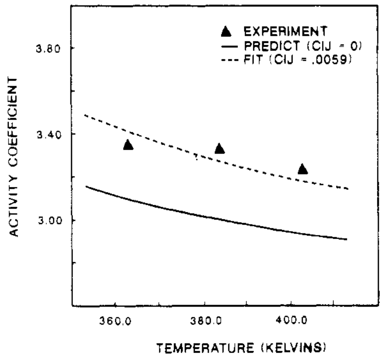

Figure 7. Infinite-dilution activity coefficients for *n*-hexane in dibenzofuran with the Peng–Robinson equation of state.

M_L	molecular weight of stationary phase, gm/mol
P	system pressure, atm
P_B	barometric pressure, atm
P°	solute vapor pressure, atm
P°_w	vapor pressure of water at room temperature, mmHg
R	gas constant, 82.05 atm cm^3/(mol·K)
t_R	net retention time, min
T	system temperature, K
T_R	room temperature, K
V	molar volume of pure liquid solute, cm^3/mol
V_g	specific retention volume, cm^3/g
V_g^∞	specific retention volume at infinite dilution, cm^3/g
V_N	net retention volume, cm^3
W	weight loading in the column
W_L	mass of the stationary phase, g

Greek Letters

γ^∞	infinite-dilution activity coefficient
γ_p^∞	uncorrected infinite-dilution activity coefficient

θ reduced sample size

Registry No. *n*-Hexane, 110-54-3; *n*-heptane, 142-82-5; *n*-octane, 111-65-9; *n*-nonane, 111-84-2; cyclohexane, 110-82-7; benzene, 71-43-2; toluene, 108-88-3; *p*-xylene, 106-42-3; 2-butanone, 78-93-3; 3-pentanone, 96-22-0; fluorene, 86-73-7; dibenzofuran, 132-64-9; *n*-hexadecane, 544-76-3.

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Thermodynamic Properties of Binary Mixtures Containing Cycloalkanones. 3. Excess Volumes of Cycloalkanones + Cyclohexane, + Benzene, and + Tetrachloromethane

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Molar excess volumes have been determined by means of a vibrating-tube densimeter for binary liquid mixtures of cycloalkanones (cyclopentanone and cyclohexanone) + cyclohexane, + benzene, and + tetrachloromethane. The V^E data are reported over the complete mole fraction range at 288.15, 298.15, and 308.15 K. The obtained excess volumes are positive for mixtures of cyclopentanone with cyclohexane and are negative for mixtures of the cycloalkanones with benzene and tetrachloromethane; for the system cyclohexanone–cyclohexane the V^E values are positive for a wide range of mole fraction, but at very low cyclohexane mole fraction an inversion of the sign of V^E is observed. The data show that in the considered range of temperature the values of the temperature coefficient ($\partial V^E/\partial T$) are negative for mixtures of the cycloalkanones with benzene and are almost zero for mixtures with cyclohexane and with tetrachloromethane.

Introduction

Table I. Experimental Measurements of Liquid Density

component	ρ_s, g cm^{-3}			
	288.15 K	298.15 K	308.15 K	lit.[a]
cyclopentanone	0.953714	0.944004	0.935958	0.94383 (*3*)
cyclohexanone	0.951130	0.942212	0.934841	0.94247 (*4*) 0.94201 (*5*)
cyclohexane	0.783120	0.773860	0.765645	0.77385 (*6*)
benzene	0.884134	0.873608	0.864327	0.87360 (*7*)
tetrachloromethane	1.603597	1.584440	1.567498	1.58439 (*8*)

[a] At 298.15 K.

This paper can be considered as a continuation of our previous studies on the excess thermodynamic properties of the binary mixtures containing cycloalkanone with organic solvents (*1*, *2*).

In the present paper we have studied mixtures of cyclopentanone or cyclohexanone with cyclohexane that present rather unspecific interaction and mixtures of these cycloalkanones with tetrachloromethane and with benzene that show specific interactions. We took a specific interest in the examination of the temperature dependence of V^E in these mixtures.

Experimental Section

Excess volumes were determined from densities measured by use of a vibrating densimeter (Model DMA 602, Anton Paar) with a reproducibility within ±1.5 × 10^{-6} g cm^{-3} at 288.15, 298.15, and 308.15 K.

The measuring cell of the apparatus was thermostated with a Heto-Birkerod ultrathermostat with an accuracy of ±0.01 K. The liquid mixtures were prepared by weight in a septum-capped vial of approximately 5-mL capacity. The two components were injected through the septum into the vial without allowing any vapor to escape, and then the sample was injected into the cell of the densimeter where its density was recorded. The temperature fluctuations in the cell were ±0.005 K during the course of a run. The mole fraction error is estimated to be less than 1 × 10^{-4}. The error limit of the density $\Delta\rho$ is estimated to be ±1 × 10^{-5} g cm^{-3}. The V^E values were accurate to ±0.003 cm^3 mol^{-1}. All liquids were of the best quality available from Fluka (AG, puriss. grade).

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