

b_i	constants in eq 2 ($i = 0, 1, 2$)
b_{0i}	constants in eq 2.1 ($i = 1, 2, 3$)
b_{1i}	constants in eq 2.2 ($i = 0, 1, 2$)
b_{20}	constant in eq 2.3
$c, d, e,$ $f, g,$ h	constants in eq 3
k	Boltzmann constant ($= 1.380622 \times 10^{-23} \text{ J}\cdot\text{K}^{-1}$)
α, γ	constants in eq 3
δ	force constant of Stockmayer 12-6-3 potential
ϵ	force constant of Stockmayer 12-6-3 potential, J
η	viscosity, $\mu\text{Pa}\cdot\text{s}$
η_1	viscosity at atmospheric pressure, $\mu\text{Pa}\cdot\text{s}$
ρ	density, $\text{kg}\cdot\text{m}^{-3}$
σ	force constant of Stockmayer 12-6-3 potential, nm

Registry No. R13B1, 75-63-8; R142B, 75-68-3; R152A, 75-37-6.

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Infinite-Dilution Activity Coefficients for Alkanals, Alkanoates, Alkanes, and Alkanones in 4-Methyl-2-pentanone

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Infinite-dilution activity coefficients are determined in a gas-liquid partition chromatograph for three alkanals, two alkanoates, four alkanes, and three alkanones in 4-methyl-2-pentanone (MIBK) as the stationary phase. The three temperatures observed are 55, 75, and 115 °C with column operating pressures up to 7.0 atm. The measured values are compared to those from two group contribution methods.

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_A^∞) are important because solution effects are usually at a maximum at infinite dilution. Data are reported in this work for 12 solutes in the stationary phase 4-methyl-2-pentanone (MIBK) at 55, 75, and 115 °C, with the column pressures from 4.5 to 7.0 atm. The solutes are alkanals, alkanoates, alkanes, and alkanones. Additionally benzene is studied for comparison with literature values.

The experimental apparatus, procedure, and data reduction have been described (1-3). The chemicals used are presented in Table I. To check our experiment at the two higher temperatures of interest, we determined data in the solvent of this work for comparison with data in the literature. Table II shows that the present result is practically identical with the literature value for the first and last points. The divergence of the second point seems not excessive in view of the extrapolation that has to be made on the literature data.

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Table I. Chemicals Used in Experimental Work

compound	source	purity
helium	Airco (purified, Grade 4.5)	99.995
argon	Airco (prepurified, Grade 4.8)	99.998
<i>n</i> -propanal	Fluka AG, Buchs SG	>99%
<i>n</i> -butanal	Eastman	research grade
<i>n</i> -pentanal	Aldrich	99%
ethyl ethanoate	Fluka AG, Buchs SG	spectrophotometric grade
ethyl propanoate	Fluka AG, Buchs SG	>99%
<i>n</i> -hexane	Aldrich	spectrophotometric grade
<i>n</i> -heptane	Aldrich	99+%
2,2,4-trimethyl-pentane	Fluka AG, Buchs SG	spectrophotometric grade
<i>n</i> -octane	Phillips	99.5% by GC
2-propanone	Fisher	99.5%
2-butanone	Baker	99.8%
2-pentanone	Aldrich	97%
4-methyl-2-pentanone (MIBK)	Aldrich	99.5%
benzene	Mallinckrodt	spectrophotometric grade

Each of Tables III, IV, and V presents the new results at one temperature of this work. For each solute we show V_g^∞ , K_A^∞ , P_A^0 , ϕ_A^0 , Poynting term, ϕ_A , and finally γ_A^∞ . The specific retention volume, V_g , is defined as the volume of gas, measured at the column temperature and pressure, needed to elute one-half of the solute from a GLPC column containing 1 g of the liquid stationary phase. This definition assumes that the peaks are symmetrical. The K value is $K_A = y_A/x_A$, where y_A and x_A are the mole fractions of the solute A in the vapor and

Table II. Comparison of GLPC Results of This Work with Literature Values

system	γ_A^∞	
	lit. value	this work
benzene in 4-methyl-2-pentanone at 75 °C	1.08 (static, extrapoltd) (4)	1.09
2-propanone in 4-methyl-2-pentanone at 115 °C	1.05 (static, extrapoltd) (5)	1.11
2-butanone in 4-methyl-2-pentanone at 115 °C	1.06 (static, extrapoltd) (6)	1.05

liquid phase. The superscript ∞ indicates that the solute is at a very low concentration. The vapor pressure is represented by P_A^0 ; ϕ_A^0 is the saturated vapor fugacity coefficient of pure component A at T ; ϕ_A is the fugacity coefficient of component A in the gas mixture at T and p . The term y_{He} is the mole fraction of helium in the gas phase. As can be seen, the carrier gas is heavily loaded with the stationary phase MIBK. The more directly determined V_g^∞ and K_A^∞ values are given so that, if better data on the other terms become available, the activity coefficients can be reevaluated readily. The terms ϕ_A^0 and ϕ_A are estimated by using second virial coefficients. The computer

Table III. Infinite-Dilution K Values and Activity Coefficients in 4-Methyl-2-pentanone at 55.0 °C

solute	$p_{\text{col}} = 4.5 \text{ atm}, y_{\text{He}} = 0.974$						
	V_g^∞	K_A^∞	$p_A^0, \text{ atm}$	ϕ_A^0	Poynting term	ϕ_A	γ_A^∞
<i>n</i> -propanal	195.8	0.306	1.265	0.9446	1.0093	0.9911	1.13
<i>n</i> -butanal	486.3	0.123	0.5072	0.9683	1.0141	0.9891	1.10
<i>n</i> -pentanal	1362.0	0.0439	0.1838	0.9831	1.0180	0.9863	1.06
ethyl ethanoate	482.0	0.124	0.4590	0.9729	1.0155	0.9903	1.22
ethyl propanoate	1112.0	0.0538	0.2040	0.9835	1.0193	0.9884	1.17
<i>n</i> -hexane	171.2	0.350	0.6360	0.9648	1.0199	0.9947	2.50
<i>n</i> -heptane	444.4	0.135	0.2283	0.9814	1.0246	0.9923	2.62
2,2,4-trimethylpentane	419.7	0.143	0.2341	0.9801	1.0277	0.9921	2.70
<i>n</i> -octane	1073.9	0.0557	0.0832	0.9902	1.0282	0.9895	2.93
2-propanone	235.8	0.254	0.9565	0.9512	1.0102	0.9897	1.23
2-butanone	555.2	0.108	0.4307	0.9709	1.0143	0.9880	1.13
2-pentanone	1172.0	0.0460	0.1887	0.9835	1.0180	0.9857	1.08

Table IV. Infinite-Dilution K Values and Activity Coefficients in 4-Methyl-2-pentanone at 75.0 °C

solute	$p_{\text{col}} = 4.7 \text{ atm}, y_{\text{He}} = 0.943$						
	V_g^∞	K_A^∞	$p_A^0, \text{ atm}$	ϕ_A^0	Poynting term	ϕ_A	γ_A^∞
<i>n</i> -propanal	116.3	0.524	2.343	0.9216	1.0066	0.9803	1.11
<i>n</i> -butanal	268.4	0.226	1.006	0.9521	1.0127	0.9761	1.07
<i>n</i> -pentanal	676.5	0.090	0.3985	0.9724	1.0174	0.9706	1.04
ethyl ethanoate	265.5	0.228	0.9314	0.9575	1.0141	0.9774	1.16
ethyl propanoate	560.0	0.108	0.4464	0.9724	1.0185	0.9735	1.12
<i>n</i> -hexane	106.8	0.569	1.212	0.9463	1.0175	0.9829	2.25
<i>n</i> -heptane	251.5	0.242	0.4761	0.9696	1.0236	0.9780	2.35
2,2,4-trimethylpentane	247.8	0.245	0.4763	0.9860	1.0266	0.9775	2.38
<i>n</i> -octane	572.4	0.106	0.1906	0.9827	1.0278	0.9726	2.52
2-propanone	136.5	0.442	1.822	0.9296	1.0081	0.9781	1.19
2-butanone	307.2	0.199	0.8621	0.9559	1.0131	0.9745	1.09
2-pentanone	659.0	0.092	0.4084	0.9731	1.0173	0.9740	1.04
benzene	306.5	0.198	0.8523	0.9690	1.0129	0.9812	1.09

Table V. Infinite-Dilution K Values and Activity Coefficients in 4-Methyl-2-pentanone at 115.0 °C

solute	$p_{\text{col}} = 7.0 \text{ atm}, y_{\text{He}} = 0.853$						
	V_g^∞	K_A^∞	$p_A^0, \text{ atm}$	ϕ_A^0	Poynting term	ϕ_A	γ_A^∞
<i>n</i> -propanal	51.12	0.885	6.478	0.8631	1.0014	0.9499	1.05
<i>n</i> -butanal	101.4	0.446	3.107	0.9073	1.0128	0.9392	1.03
<i>n</i> -propanal	211.8	0.214	1.414	0.9396	1.0215	0.9263	1.02
ethyl ethanoate	98.61	0.459	3.005	0.9120	1.0143	0.9408	1.09
ethyl propanoate	182.70	0.248	1.599	0.9372	1.0225	0.9309	1.05
<i>n</i> -hexane	50.90	0.889	3.498	0.8950	1.0169	0.9481	1.85
<i>n</i> -heptane	102.5	0.442	1.586	0.9331	1.0290	0.9360	1.90
2,2,4-trimethylpentane	104.2	0.435	1.529	0.9317	1.0329	0.9342	1.93
<i>n</i> -octane	202.4	0.224	0.7365	0.9570	1.0369	0.9230	1.98
2-propanone	58.03	0.780	5.310	0.8724	1.0046	0.9452	1.11
2-butanone	112.6	0.402	2.691	0.9146	1.0140	0.9361	1.05
2-pentanone	212.9	0.213	1.439	0.9416	1.0214	0.9269	0.996

Table VI. Comparison of Experimental Infinite-Dilution Activity Coefficients with Values Predicted by NTGC and UNIFAC Methods

solute	temp., °C	$\gamma_A^\infty(\text{expt})$	NTGC Model		revised parameters		original parameters	
			γ_A^∞	% diff	γ_A^∞	% diff	γ_A^∞	% diff
<i>n</i> -propanal	55	1.13			0.965	-14.6	0.968	-14.3
	75	1.11			0.960	-13.5	0.947	-14.7
	115	1.05			0.952	-9.3	0.914	-13.0
<i>n</i> -butanal	55	1.10			0.972	-11.6	0.953	-13.4
	75	1.07			0.968	-9.5	0.938	-12.3
	115	1.03			0.961	-6.7	0.913	-11.4
<i>n</i> -pentanal	55	1.06			0.988	-6.8	0.944	-10.9
	75	1.04			0.983	-5.5	0.933	-10.3
	115	1.02			0.976	-4.3	0.916	-10.2
ethyl ethanoate	55	1.22			1.05	-13.9	1.15	-5.7
	75	1.16			1.06	-8.6	1.14	-1.7
	115	1.09			1.07	-1.8	1.12	2.8
ethyl propanoate	55	1.17			1.10	-6.0	1.15	-1.7
	75	1.12			1.11	-0.9	1.15	2.7
	115	1.05			1.12	6.7	1.14	8.6
<i>n</i> -hexane	55	2.50	2.31	-7.6	2.32	-7.2	1.92	-23.2
	75	2.25	2.17	-3.6	2.23	-0.9	1.90	-15.7
	115	1.85	1.95	-5.4	2.07	11.9	1.86	0.5
<i>n</i> -heptane	55	2.62	2.47	-5.7	2.60	-0.8	2.09	-20.4
	75	2.35	2.30	-2.1	2.48	5.5	2.06	-12.3
	115	1.90	2.04	7.4	2.28	20.0	2.01	5.8
2,2,4-trimethylpentane	55	2.70	2.85	5.6	2.90	7.4		
	75	2.38	2.62	10.1	2.74	15.1		
	115	1.93	2.28	18.1	2.49	29.0		
<i>n</i> -octane	55	2.93	2.63	-10.2	2.87	-2.0	2.24	-23.7
	75	2.52	2.42	-4.0	2.72	7.9	2.21	-12.3
	115	1.98	2.13	7.6	2.47	24.7	2.15	8.6
2-propanone	55	1.23	1.07	-13.0	1.04	-15.4	0.970	-21.1
	75	1.19	1.06	-10.9	1.03	-13.4	0.970	-18.5
	115	1.11	1.04	-6.3	1.02	-8.1	0.970	-12.6
2-butanone	55	1.13	1.02	-9.7	1.01	-10.6	0.988	-12.5
	75	1.09	1.02	-6.4	1.01	-7.3	0.988	-9.4
	115	1.05	1.01	-3.8	1.01	-3.8	0.988	-5.9
2-pentanone	55	1.08	0.997	-7.7	1.00	-7.4	0.997	-7.7
	75	1.04	0.997	-4.1	1.00	-3.8	0.997	-4.1
	115	0.996	0.996	0.0	1.00	0.4	0.997	0.1
benzene	75	1.09			0.91	-16.5	1.10	0.9

programs and numerical values for the data reduction are given elsewhere (2).

Based on uncertainties in the mass of the stationary phase on the column, carrier gas flow rate, retention time determination, calculation of y_{He} , pressure, and temperature, the relative error in the K values was estimated to be $\pm 1.04\%$. The accuracy of the activity coefficients is believed to be within 2.4%. The GLPC timer measures the peak maximum retention time only for symmetrical peaks (1). Over 70% of the peaks were symmetrical with skews in the range of 0.8–1.2. About 4% had skews outside the range of 0.7–2.0, with the maximum range being 0.6–3.7. All retention times for peaks with skews outside the range of 0.8–1.2 were corrected to the peak maximum retention. This and surface effects, as discussed elsewhere (2, 3, 7, 8), may add additional error.

Table VI is a comparison of measured activity coefficients of this work with predictions by group contribution methods. Two predictive methods were chosen. One is the NTGC model (9, 10) and the other is the UNIFAC model (11, 12). The parameters for the NTGC model are published elsewhere (2, 9) and are based on vapor–liquid equilibrium data other than the infinite-dilution activity coefficients reported here. The revised and original UNIFAC parameters were used for comparison with the experimental limiting activity coefficients. The agreement is acceptable, with the revised parameters being slightly better. The NTGC method, which also gives density, heat of vaporization, and excess enthalpy, is slightly better than the UNIFAC values. Neither method has the same temperature dependence as the experimental data.

Registry No. 4-Methyl-2-pentanone, 108-10-1; propanal, 123-38-6; pentanal, 110-62-3; ethyl ethanoate, 141-78-6; butanal, 123-72-8; ethyl propanoate, 105-37-3; *n*-hexane, 110-54-3; *n*-heptane, 142-82-5; 2,2,4-trimethylpentane, 540-84-1; *n*-octane, 111-65-9; 2-propanone, 67-64-1; 2-butanone, 78-93-3; 2-pentanone, 107-87-9.

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