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Infinite-Dilution Activity Coefficients for Alkanals, Alkanoates, Alkanes, and Alkanones in *n*-Octane

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Infinite-dilution activity coefficients are determined in a gas-liquid partition chromatograph for four alkanals, three alkanoates, three alkanes, and four alkanones in *n*-octane as the stationary phase. The three temperatures observed are 55, 75, and 115 °C with column operating pressures up to 6.9 atm.

The activity coefficient is an important and fundamental thermodynamic property of liquid mixtures. It is a measure of the deviation from ideality of a component's behavior in a mixture. Activity coefficients at infinite dilution are important because solution effects are usually at their maximum at infinite dilution. The infinite-dilution activity coefficient values are useful for predicting vapor-liquid equilibrium compositions over the entire concentration range, provided that the activity coefficients vary monotonically with mole fraction (*1*).

Data are reported in this work for 16 solutes in the stationary phase *n*-octane at 55, 75, and 115 °C with the column pressures at 2.9 and 6.9 atm. The solutes are alkanals, alkanoates, alkanes, and alkanones. Additionally, benzene and carbon tetrachloride are studied for comparison with literature values.

The experimental apparatus and procedures have been described (*2*, *3*). The vapor-liquid equilibrium ratio K_A for the solute A is determined from experimentally observed variables of a gas-liquid partitions chromatograph as follows:

$$K_a = \left(\frac{m_s}{W_s}\right)\left(\frac{1}{F_a}\right)\left(\frac{60}{t_{RA} - t_G}\right)(294.2 z_a R) y_{He} \quad (1)$$

where $K_A = y_A/x_A$. The mole fractions of component A in the vapor and the liquid are represented by y_A and x_A, respectively. The mass and the molecular weight of the liquid stationary phase in the GLPC column are given by m_s and W_s. F_a is the volumetric flow rate of the helium carrier gas in cm^3/min measured at the ambient conditions of 21 °C and 1 atm. The retention times in seconds, t_{RA} and t_G, are for the pure solute A and a hypothetical insoluble gas. The retention time of argon is used to approximate t_G. z_a is the compressibility of the pure helium carrier gas at the ambient conditions, R is the gas constant, and y_{He} is the mole fraction of the helium in the gas mixture inside the GLPC column. The specific retention volume, V_g is defined as the volume of gas needed to elute one-half of the solute from the GLPC column containing 1 g of the liquid stationary phase measured at the column temperature and pressure. V_g is obtained from the experimentally observed quantities by

$$V_g = \left(\frac{F_a}{m_s}\right)\left(\frac{t_{RA} - t_G}{60}\right)\left[\left(\frac{z_m}{z_a}\right)\left(\frac{1}{p}\right)\left(\frac{T}{294.2}\right)\right] y_{He} \quad (2)$$

where T and p are the GLPC column temperature and pressure and z_m is the compressibility of the gas mixture in the GLPC column. The K value at infinite dilution can be calculated from the specific retention volume at infinite dilution by the expression

$$K_A^\infty = z_m RT/(V_g^\infty p W_s) \quad (3)$$

Table I. Chemicals Used in Experimental Work

compd	source	purity
helium	Airco (purified, Grade 4.5)	99.995
argon	Airco (prepurified, Grade 4.8)	99.998
propanal	Fluka AG, Buchs SG	⩾99%
butanal	Eastman	research grade
pentanal	Aldrich	99%
hexanal	Aldrich	99%
ethyl ethanoate	Fluka AG, Buchs SG	spectrophotometric grade
ethyl propanoate	Fluka AG, Buchs SG	⩾99%
ethyl butanoate	Fluka AG, Buchs SG	⩾98%
n-pentane	Aldrich	99+%
n-hexane	Aldrich	spectrophotometric grade
2,2,4-trimethylpentane	Fluka AG, Buchs SG	spectrophotometric grade
n-octane	Phillips	99.5% by GC
2-propanone	Fisher	99.5%
2-butanone	Baker	99.8%
2-pentanone	Aldrich	97%
4-methyl-2-pentanone	Aldrich	99.5%
benzene	Mallinckrodt	spectrophotometric grade
carbon tetrachloride	Mallinckrodt	spectrophotometric grade

where the superscript ∞ refers to the fact that the values of y_A and x_A are approaching zero. Activity coefficients at infinite dilution can be determined from the K_A^∞ values by using the equation

$$\gamma_A^\infty = p\phi_A K_A^\infty / \{p_A^0 \phi_A^0 \exp[(p - p_A)V_A/RT]\} \quad (4)$$

ϕ_A is the fugacity coefficient of component A in the gas mixture at T and p, ϕ_A^0 is the saturated vapor fugacity coefficient of pure component A at T, V_A is the molar volume of the pure liquid A at T, and p_A^0 is the pure-component vapor pressure of the solute at T.

The volatile stationary phase, *n*-octane, was kept on the GLPC column packing by presaturating the carrier gas, operating at elevated pressures, and using low flow rates to minimize the pressure drop. Pressure drops were measured for each run and varied between 0.014 and 0.027 atm. The presaturator temperature, system pressure, and carrier gas flow could be adjusted so that at steady state the GLPC column either gained or lost the liquid stationary phase at a slow rate. This gain or loss was determined by repeated injection of a reference solute (*3*) at regular intervals, and interpolation of the results in between the intervals. However, during start-up and shutdown, 3-5% of the volatile stationary phase was usually removed from the GLPC column. Valves were installed on the inlet and the outlet of the GLPC column that could be quickly opened and closed at the beginning and the end of a run to prevent loss of the stationary phase during start-up and shutdown.

Obtaining infinite dilution requires sample sizes for each solute on the order of 0.1 μL of liquid (*4*). Long retention times were unavoidable because reducing the weighing error in m_s necessitated fairly heavily loaded GLPC column packing and

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

system	γ_A^∞	
	lit. value	this work
benzene in *n*-octane at 55 °C	1.40 (static) (*6, 7*)	1.39
carbon tetrachloride in *n*-octane at 55 °C	1.12 (static) (*8*)	1.11
benzene in *n*-octane at 75 °C	1.29 (static) (*7*)	1.30

reducing the GLPC column pressure drop required low flow rates. These long retention times coupled with the noisy base line generated by a saturated carrier gas made timing of small samples difficult. Sample sizes of pure components in the range of 0.5–3.0 µL were used and the results extrapolated to zero sample size using peak areas. Blended samples larger than 3.0 µL were sometimes used, but only when good resolution was achieved. With the heaviest solutes at the lowest temperature, it was occasionally necessary to extend the maximum pure-solution sample size past 3.0 µL.

With polar–nonpolar systems and samples of this size, fronting peaks are produced that in exceptional cases can give a skew of 3.0, but in general ranged from 0.7 to 2.0. The GLPC timer measures the peak maximum retention time only when symmetrical peaks are produced (*2*). All retention times for peaks with skews outside the range 0.8–1.2 were corrected for the peak maximum retention time by extrapolation to zero sample size.

Table III. Infinite-Dilution *K* Values and Activity Coefficients in *n*-Octane at 55.0 °C[a]

solute	V_g^∞	K_A^∞	p_A^0, atm	ϕ_A^0	Poynting term	ϕ_A	γ_A^∞
propanal	53.64	1.52	1.265	0.9446	1.0047	0.9945	3.64
butanal	148.8	0.547	0.5072	0.9683	1.0084	0.9930	3.18
pentanal	422.7	0.193	0.1838	0.9831	1.0113	0.9909	3.03
hexanal	1310.0	0.0621	0.0701	0.9909	1.0136	0.9886	2.53
ethyl ethanoate	184.5	0.441	0.4590	0.9729	1.0094	0.9928	2.82
ethyl propanoate	511.1	0.159	0.2040	0.9835	1.0121	0.9913	2.25
ethyl butanoate	1227.3	0.0663	0.0998	0.9892	1.0145	0.9894	1.90
n-pentane	128.3	0.634	1.832	0.9355	1.0049	0.9956	1.07
n-hexane	363.5	0.224	0.6360	0.9648	1.0116	0.9936	1.07
2,2,4-trimethylpentane	911.3	0.0893	0.2341	0.9801	1.0172	0.9914	1.10
2-propanone	51.14	1.59	0.9565	0.9512	1.0056	0.9938	4.91
2-butanone	146.5	0.555	0.4307	0.9709	1.0086	0.9924	3.79
2-pentanone	371.9	0.219	0.1887	0.9835	1.0113	0.9907	3.35
4-methyl-2-pentanone	728.8	0.112	0.1155	0.9866	1.0136	0.9897	2.78
benzene	395.8	0.206	0.4302	0.9803	1.0085	0.9920	1.39
carbon tetrachloride	435.2	0.187	0.4909	0.9774	1.0091	0.9922	1.11

[a] $T_{col} = 55.0$ °C, $p_{col} = 2.9$ atm, $y_{He} = 0.971$.

Table IV. Infinite-Dilution *K* Values and Activity Coefficients in *n*-Octane at 75.0 °C[a]

solute	V_g^∞	K_A^∞	p_A^0, atm	ϕ_A^0	Poynting term	ϕ_A	γ_A^∞
propanal	36.42	2.37	2.343	0.9216	1.0016	0.9865	3.13
butanal	91.66	0.941	1.006	0.9521	1.0065	0.9832	2.78
pentanal	237.1	0.364	0.3986	0.9724	1.0102	0.9792	2.64
hexanal	641.0	0.134	0.1659	0.9839	1.0127	0.9746	2.30
ethyl ethanoate	113.3	0.761	0.9314	0.9575	1.0073	0.9828	2.42
ethyl propanoate	282.5	0.305	0.4464	0.9724	1.0107	0.9795	1.98
ethyl butanoate	641.5	0.134	0.2244	0.9816	1.0134	0.9759	1.71
n-pentane	82.59	1.05	3.198	0.9085	0.9987	0.9872	1.06
n-hexane	208.0	0.415	1.212	0.9463	1.0084	0.9831	1.04
2,2,4-trimethylpentane	502.3	0.172	0.4763	0.9680	1.0152	0.9785	1.06
2-propanone	34.30	2.51	1.822	0.9296	1.0030	0.9853	4.23
2-butanone	90.86	0.950	0.8621	0.9559	1.0069	0.9824	3.26
2-pentanone	214.8	0.402	0.4084	0.9731	1.0100	0.9792	2.84
4-methyl-2-pentanone	380.1	0.227	0.2597	0.9774	1.0124	0.9767	2.50
benzene	227.6	0.379	0.8523	0.9690	1.0068	0.9825	1.30

[a] $T_{col} = 75.0$ °C, $p_{col} = 2.9$ atm, $y_{He} = 0.933$.

Table V. Infinite-Dilution *K* Values and Activity Coefficients in *n*-Octane at 115.0 °C[a]

solute	V_g^∞	K_A^∞	p_A^0, atm	ϕ_A^0	Poynting term	ϕ_A	γ_A^∞
propanal	19.27	2.10	6.478	0.8631	1.0011	0.9642	2.49
butanal	42.29	0.955	3.107	0.9073	1.0125	0.9562	2.21
pentanal	90.27	0.447	1.414	0.9396	1.0211	0.9466	2.15
hexanal	201.90	0.200	0.6751	0.9603	1.0276	0.9360	1.94
ethyl ethanoate	47.98	0.842	3.005	0.9120	1.0139	0.9550	2.00
ethyl propanoate	102.6	0.393	1.599	0.9372	1.0221	0.9471	1.70
ethyl butanoate	206.8	0.195	0.8437	0.9572	1.0290	0.9388	1.52
n-pentane	38.25	1.06	8.083	0.8390	0.9948	0.9648	1.04
n-hexane	81.83	0.493	3.498	0.8950	1.0165	0.9548	1.02
2,2,4-trimethylpentane	176.1	0.229	1.530	0.9317	1.0323	0.9434	1.01
2-propanone	17.71	2.28	5.310	0.8724	1.0043	0.9612	3.25
2-butanone	41.08	0.983	2.691	0.9146	1.0137	0.9543	2.59
2-pentanone	82.32	0.490	1.440	0.9416	1.0210	0.9468	2.32
4-methyl-2-pentanone	133.5	0.302	0.9670	0.9490	1.0267	0.9408	2.08
benzene	89.63	0.450	2.611	0.9359	1.0136	0.9545	1.20

[a] $T_{col} = 115.0$ °C, $p_{col} = 6.9$ atm, $y_{He} = 0.887$.

The GLPC column preparation has been described (*2*, *3*). Several columns from 10 to 24 in. in length were used. The packings were Chromosorb HP 60/80 mesh, Chromosorb w HP 90/100 mesh, and 40/50 mesh Anakrom C-22 acid-washed firebrick. The Chromosorb packing showed practically no tailing for the polar solutes.

The three predominant retention mechanisms that can occur in a GLPC column are (1) partitioning of the solute between the gas and the liquid phase, (2) solute adsorption at the gas-liquid interface, and (3) solute adsorption on the surface of the packing. The last two retention mechanisms need to be eliminated in order to measure bulk solution thermodynamic properties. Solute adsorption on the surface of the packing can be avoided by using columns with at least 15-20% liquid loading on deactivated solid supports (*5*). Surface effects in this work are avoided by using an inactive packing, high liquid loading (20-30%), and small but finite samples and extrapolating to zero sample size.

The chemicals used are presented in Table I. Because chromatography is a separation technique, extremely pure solute samples are not required. The purity of the solvent, *n*-octane, was checked by GC. Table II is a comparison of GLPC values obtained with literature values. The GLPC results for each of the three temperatures are listed in Tables III-V. The accuracy of the activity coefficients is believed to be within 2.4%. The relative error in the *K* value was estimated to be ±1.04%.

For each solute in Tables III-V, V_g^∞, K_A^∞, p_A^0, ϕ_A^0, the Poynting term, ϕ_A, and γ_A^∞ are listed. 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 coefficient can be readily reevaluated. The terms ϕ_A^0 and ϕ_A are estimated by using second virial coefficients. The computer programs for the data reduction calculations are given elsewhere (*3*).

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Yonghui Liu repeated the experiments and confirmed the results at 55 °C for *n*-pentane, *n*-hexane, carbon tetrachloride, and benzene.

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Viscosity Studies of Some Binary Liquid Systems

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Viscosity and density data are presented for six binary solvent mixtures at 20 °C over the entire range of composition. The experimental data are compared with literature values and fitted to several empirical relations proposed by McAllister, Heric, and Auslander and also to a polynomial equation using a multiparametric curve-fitting program. Further, an attempt has been made to test the validity of these relations based on the experimental data.

Introduction

In recent years there has been renewed interest in the study of thermodynamic, hydrodynamic, and optical properties of binary liquid mixtures (*1-8*). Among the various hydrodynamic properties, the literature dealing with systematic studies of the viscosity of mixtures is rather limited. A number of empirical relations (*9-15*) have been proposed to predict the viscosity of a mixture from that of pure components. In an attempt to test the validity of these relations, we have undertaken to measure the viscosity of six solvent mixtures comprising benzene (B), cyclohexane (CH), ethyl acetate (EA), and carbon tetrachloride (CCL). These binary data were fitted to the empirical relations of McAllister (*11*), Herric (*15*), and Auslander (*13*) and also to a polynomial equation using a multiparametric curve-fitting program.

Theories of Liquid Viscosity

Several theories have been put forth relating the viscosity of pure components to their mixtures. They are as follows.

***Eyring's Theory* (*9,10*).** One of the earliest theories of liquid viscosity due to Eyring and co-workers may be written as

$$\eta = (hN/M)\exp(\Delta G^*/RT) \qquad (1)$$

Here, η is viscosity, M is the molecular weight, T is the absolute temperature, and h, N, and R are Planck's constant, Avogadro's number, and the gas constant, respectively. ΔG^* represents the free energy of activation for viscous flow. The excess free energy of activation, ΔG^{*E}, is given by the difference between the free energy of activation of the mixture and the free energy of activation of the ideal mixture. Thus, from eq 1

$$\Delta G^{*E} = RT(\ln \eta\bar{M} - X_1 \ln \eta_1 M_1 - X_2 \ln \eta_2 M_2) \qquad (2)$$

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