Table I. Densities d of 2-Butoxyethanol at Different Temperatures t

	$d/(\mathrm{g\ cm^{-3}})$			
t/°C	densimeter	eq 1	pycnometer	lit.
20.00		0.9004	0.9005	0.900 75[a]
27.00		0.8946		0.894 60[b]
29.99	0.892 07	0.8920		
30.00		0.8920	0.8920	0.892 36[a]
40.00		0.8835	0.8835	0.883 89[a]
40.01	0.883 51	0.8835		
44.98	0.879 30	0.8793		
45.00		0.8792	0.8792	
49.99	0.874 92	0.8749		
50.00		0.8749	0.8750	
54.00		0.8715	0.8715	
60.00		0.8662	0.8662	0.866 59[a]

[a] Reference 7. [b] Reference 5.

packed with Raschig rings. The organic impurity level, as estimated by gas-liquid chromatography using an FFAP column and flame ionization detection, was less than 0.03 mol %; the major contaminants were 1-butanol and 1,2-ethanediol. The water impurity level, as estimated by gas-liquid chromatography using a Polypak column and thermal conductivity detection, was less than 0.02 mol %. The refractive index n^{20}_{D} was found to be 1.419 81 ± 0.000 05, in excellent agreement with the value 1.4198 quoted in ref *2* but slightly higher than the values reported for two different samples by Schneider and Wilhelm, 1.4194 and 1.4196 (*3*).

Two sets of density measurements were carried out. For the first set an Anton Paar 02C densimeter was used. It was calibrated by using water and air. The water was distilled, passed through an ion-exchange column, and degassed by vigorous boiling; its density was taken from the work of Kell (*4*). The density of air was obtained from tables (*2*), its temperature, pressure, and relative humidity being known. The temperature was measured to ±35 mK by using a thermistor calibrated against a platinum resistance thermometer bearing a certification from the British Calibration Service. Scatchard and Wilson (*5*) found that air-saturated 2-butoxyethanol has a rather higher density than the degassed liquid and thus our samples were boiled vigorously before measurement to expel dissolved gas. Our results therefore correspond to essentially 1-atm pressure. Column 2 of Table I contains the results of this set of measurements; we estimate their precision to be ±0.000 03 g cm^{-3}. The second set of measurements was made by using a Pyrex pycnometer having a bulb of about 6.5-cm^3 capacity and a capillary of bore 1.500_4 mm; it was calibrated by using mercury whose density was taken from ref *6*. The temperature was determined to ±3 mK by using the platinum resistance thermometer mentioned above. The liquid was sealed under its own vapor pressure by a grease-free stopcock sealed to the top of the capillary. Our densities from this set of measurements are thus orthobaric. They are listed in column 4 of Table I; we estimate their precision to be ±0.0001 g cm^{-3}. Although the results of the two series of determinations refer to slightly different pressures, they are equally well described by

$$d/(\mathrm{g\ cm^{-3}}) = 0.91694 - (8.149 \times 10^{-4})(t/{}^\circ\mathrm{C}) - (5.1 \times 10^{-7})(t/{}^\circ\mathrm{C})^2$$

$$\sigma = 3 \times 10^{-5}\ \mathrm{g\ cm^{-3}} \qquad (1)$$

where d is the density at temperature t. Values calculated from eq 1 are listed in column 3 of Table I. The good agreement with the experimental values demonstrates the concordance of both data sets. Column 5 contains literature data. The single value at 27 °C reported by Scatchard and Wilson is in excellent agreement with our value interpolated by using eq 1; these authors used essentially the same purification procedure as we used. The four values of Onken (*7*) are in poor agreement with our values. This discrepancy in d and the previously mentioned discrepancy in n^{20}_{D} are consistent with the presence of a small amount of water contamination in his samples. The effect of this would be to lower the refractive index and raise the density in the way observed.

Glossary

d	density, g cm^{-3}
t	temperature, °C
σ	standard deviation

Literature Cited

(1) Guzman, F.; McLure, I. A. *Int. Data Ser. B* **1980**, 109.
(2) Weast, R. C., Ed. "Handbook of Chemistry and Physics", 55th ed.; CRS Press: Cleveland, OH, 1974; p C290.
(3) Schneider, G.; Wilhelm, G. *Z. Phys. Chem.* **1959**, *20*, 219-32.
(4) Kell, G. S. *J. Chem. Eng. Data* **1975**, *20*, 97-105.
(5) Scatchard, G.; Wilson, C. M. *J. Am. Chem. Soc.* **1964**, *86*, 133-7.
(6) Kaye, G. W. C.; Laby, T. H. "Tables of Physical and Chemical Constants"; Longman: London, 1971; p 30.
(7) Onken, U. *Z. Elektrochem.* **1959**, *63*, 321-7.

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Limiting Activity Coefficients of Nonpolar and Polar Solutes in both Volatile and Nonvolatile Solvents by Gas Chromatography

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Limiting activity coefficients were measured for 35 solutes in 34 different solvents by gas chromatography. The data cover industrially important compounds with wide ranges of polarity, polarizability, and degree of association. Both volatile and nonvolatile solvents were studied. The data compare well with those determined from ebulliometry, those extrapolated from classical vapor-liquid equilibrium (VLE) studies, and those of other researchers using similar techniques.

Introduction

Infinite-dilution activity coefficients (γ^∞) have found numerous applications in characterizing solution behavior. They can be used to generate accurate binary parameters for several solution models (*1-3*), to predict the existence of an azeotrope (*4*), and to estimate mutual solubilities. In addition they can be used to calculate kinetic solvent effects with the Bronsted-Bjerrum relationship (*5*) as well as to provide incisive information for the statistical thermodynamicist in the absence of so-

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Table I. Designations and Pertinent Information on the Solvents and Packings Used

				ref value used^a						
	solvent	T, °C	packing	solute	γ^∞	T, °C	ref	solvent source	distilled	dried
A	acetonitrile	20	Teflon	acetone	1.05	45	*2*	Mallinckrodt AR	no	no
B	acetophenone	20	Chrom W	cyclohexane	4.34	25	*17*	Aldrich	yes	sieved
C	aniline	20	Teflon	benzene	2.23	25	*45*	Fisher Reagent	yes	sieved
D	anisole	20	Chrom W	benzene	1.05	25		Aldrich 99%	yes	sieved
E	benzene	20	Chrom W	cyclohexane	1.66	25	*46*	Fisher Reagent	yes	$CaCl_2$
F	benzonitrile	20	Chrom W	isoprene	2.07	25	*17*	Aldrich 99%	yes	sieved
G	benzyl acetate	25	Chrom W	weighing				Mallinckrodt AR	no	no
H	benzyl chloride	20	Chrom W	dichloromethane	0.85	20		Mallinckrodt AR	no	sieved
I	bromoanisole	25	Chrom W	weighing				Baker	no	no
J	bromonaphthalene	25	Chrom W	weighing				Eastman	no	no
K	butanol	20	Chrom W	pentane	4.06	25	*17*	Mallinckrodt AR	no	no
L	butanone	20	Teflon	CCl_4	1.52	55	*46*	Eastman	yes	$CaCl_2$
M	butyl chloride	20	Chrom W	weighing				Eastman	yes	$CaCl_2$
N	CCl_4	20	Chrom W	acetone	2.88	43	*20*	Fisher Reagent	no	no
O	cyclohexanone	20	both	weighing				Aldrich 99.8%	yes	Na_2SO_4
P	1,2-dichloroethane	20	both	CCl_4	1.69	64	*20*	Mallinckrodt AR	yes	K_2CO_3
Q	dimethylformamide	20	Chrom W	heptane	25.0	35	*47*	Mallinckrodt AR	no	sieved
R	ethyl acetate	20	both	hexane	3.09	35	*20*	Aldrich 99.5%	no	no
S	ethyl alcohol	20	Teflon	acetone	2.27	49	*20*	U.S. Industrial	no	no
T	heptane	20	Chrom W	hexane	1.00	20		Phillips Spectral	no	no
U	isooctane	20	Chrom W	pentane	0.98	20		Phillips Spectral	no	no
V	nitrobenzene	20	both	weighing				Fisher Reagent	no	no
W	nitroethane	20	both	benzene	1.80	25	*46*	Fisher Reagent	yes	sieved
X	nitromethane	20	both	benzene	3.84	25	*46*	Mallinckrodt AR	no	no
Y	2-nitropropane	20	Chrom W	cyclohexane	4.71	45	*48*	Aldrich 98%	no	sieved
Z	octane	20	Chrom W	pentane	0.97	20		Burdick and Jackson	no	no
AA	octanol	20	Chrom W	butanone	1.94	25	*49*	Fisher Reagent	no	no
BB	phenol	50	Chrom W	heptane	15.4	50	*50*	Mallinckrodt AR	no	no
CC	propionitrile	20	both	isopentene	4.48	25	*51*	Eastman	yes	P_2O_5
DD	propiophenone	25	Chrom W	weighing				Aldrich 99%	no	no
EE	quinoline	25	Chrom W	weighing				Eastman	no	no
FF	toluene	20	both	benzene	0.99	20		Mallinckrodt AR	no	no
GG	water	20	Chrom W	benzene	2200	25	*44*	Local (distilled)	yes	no
HH	*p*-xylene	20	both	benzene	0.99	20		Eastman	no	no

^{a} Moles of solvent on the column determined either by weighing the column before and after the solvent was added (nonvolatile solvents) or by using a reference value of γ^∞ for a given solute. If the latter, the reference solute and value and temperature of the previously determined or estimated γ^∞ are given.

lute–solute interactions. While these applications have been known for some time, the widespread use of γ^∞ has been limited by the paucity of accurate γ^∞ data available. To help alleviate this problem, we extended the gas-chromatographic technique to measure γ^∞'s for many industrially important systems.

Background

Determining γ^∞'s by gas chromatography entails measuring the retention behavior of a solute in an inert carrier gas stream passing through a column containing a solvent-coated solid support. The technique has been in existence some time and its details of operation may be found in a number of sources (*1*, *6*–*19*).

There are several advantages in using the gas chromatograph for measuring infinite-dilution activity coefficients. First, it is the only method in which γ^∞ may be found directly. Secondly, commercially available equipment can be used and the techniques are well established. Further, although solvent purity is crucial, solute purity is not critical as separation is achieved by the chromatograph. Finally, the method is by far the quickest available. Up to 30 data points may be measured in the course of a day's run. Conventional static techniques may take hours or days to obtain one or two limiting coefficients, and even the ebulliometric technique discussed in a different paper (*20*) can measure only four values in a day's run with existing equipment.

Some questions as to the general applicability of the gas-chromatographic technique have been raised. Martire (*21*) has argued that, since the liquid coating on the column is usually rather thin, there is an abnormally high surface area to volume ratio. With highly polar solvents, nonpolar solute molecules are squeezed out of the bulk phase and into the surface layer leading to surface excesses. However, calculations have been made (*22*) which showed that the depth of the interfacial layer is very much smaller than the bulk solution, implying that the overall concentrations would not be significantly affected for the liquid loadings of this study. Attention has also been focused on the adsorption of solute by the solid substrate (*23*–*25*). This problem is characterized by skewed peaks and effluent retention time dependent upon sample size. However, it was noted that it generally is easy to load the column with enough solvent so that interactions with the substrate are negligible compared to those with the solvent (*22*). Another problem which has recently drawn some attention is that of interaction of the solvent with the substrate affecting the retention time (e.g., ref *24*, *26*, and *27*). However, this problem is certainly negligible for the packings used in this study.

More serious problems are encountered when solvents nearly as volatile as the solutes are used. Most early work used very nonvolatile solvents such as squalane (*28*), octadecane (*29*), and quinoline (*30*). Two problems are encountered when a volatile solvent is used. First, in spite of presaturation of the carrier gas, some solvent is stripped off the packing because of gas-phase expansion. This can be standardized and corrected by injecting the same solute at the beginning and the end of each run and the effect minimized by running at low pressure drops. A more serious problem involves the saturation of carrier gas with solvent. The thermal conductivity detector used in these experiments functions on the principle that a solute molecule is able to change the heat-transfer characteristics of

Table II. Limiting Activity Coefficients Determined by Gas-Liquid Chromatography[a]

	γ^∞																
	A	B	C	D	E	F	G	H	I	J	K	L	M	N	O	P	Q
carbon tetrachloride	6.67	1.70	4.80	1.30	1.13		1.41		1.50	1.57	2.67	1.65			1.10	1.98	
chloroform	1.49	0.58	1.50	0.68	0.81		0.51	0.83	0.43	1.13	1.20		0.93	1.16	0.31	1.06	
methylene chloride		0.62	1.41	0.77	0.92	0.70		0.85			1.86	0.51	1.02	1.58	0.39	1.02	
methyl iodide	3.86	1.23	2.83	1.14	1.15	1.41	1.13	1.09	1.23	1.24	3.05	1.45	1.31	1.37	1.05	1.34	1.65
nitromethane											9.1		5.4	15.2			
methanol		3.47	2.39	11.0		4.7		13.9									
carbon disulfide	12.4	2.05	3.53	1.62	1.48	2.33		1.60			3.14	3.04	1.56	1.21	1.87	2.58	4.36
acetonitrile		1.65		2.26	3.47		1.51		2.75	4.4	5.67			13.4	1.43		
1,2-dichloroethane							0.71		1.13	1.43	2.92						
ethyl bromide	2.88	1.18	2.14	1.08	1.01	1.33	1.02	1.03	1.20	1.23	2.66	1.14	1.02	1.25	0.96	1.18	1.65
ethyl iodide	5.14	1.42	2.83	1.12	1.12	1.58	1.32		1.28	1.22	3.44	1.58	1.29	1.35	1.13	1.38	2.36
nitroethane																	
ethanol		3.62		10.0		4.7		12.1									
propionitrile											5.20			7.20			
acetone	1.10		0.80		1.71		1.12		1.39	2.13	2.4	1.05	1.70	3.19	1.26	0.76	
n-propyl chloride	3.36	1.39	2.96	1.14	1.06		1.22	1.22	1.41	1.49	2.88	1.18	1.02	1.26	1.06	1.35	
tetrahydrofuran																	
butanone																	
ethyl acetate	1.58		1.44	1.08			1.00		1.19	1.82					1.26		
tert-butyl chloride	4.26		4.82		1.27		1.68	1.48	1.84	2.14		1.45	1.00		1.31	1.49	
isoprene	6.03	1.92	5.27	1.54	1.24	2.12	1.68	1.90	1.78	2.06	2.91	1.50		1.00	1.48	1.68	2.98
cyclopentadiene							2.18		2.47	2.56							
1-pentene		3.68	10.4	2.43	1.72	3.62		2.62			3.54	2.52			2.59	2.92	8.00
isopentene		2.82	8.61	2.25	1.67	3.10		2.28			3.43	2.36			2.43	2.72	6.67
pentane		6.00	20.1	3.64	2.25	6.08		4.10			4.30	3.66			3.97	4.79	16.7
chlorobenzene																	
benzene	3.19		2.24	1.05			1.04		1.14	1.39				1.10	0.93		
cyclohexane		4.40	13.6	3.10	1.69	4.92	3.45		3.02	2.80	4.01		1.62	1.12	3.08	3.94	13.1
hexane		6.84	25.7	3.94	2.21	6.68	5.28	4.40	4.26	4.90	5.00	4.30	1.73	1.33	4.46	5.04	20.8
isopropyl ether							2.43		2.29	2.49				1.04			
triethylamine	11.1											2.79			2.59	2.14	
toluene																	
methylcyclohexane		4.63	17.5														16.4
heptane		7.58	31.8	4.25		7.53					7.00						26.5
isooctane			39.4														30.1

	γ^∞																
	R	S	T	U	V	W	X	Y	Z	AA	BB	CC	DD	EE	FF	GG	HH
carbon tetrachloride	1.31		1.20		2.26	3.93	8.81	2.40		1.74	3.40	3.14	1.53	1.44	1.02	6300	0.93
chloroform			1.47	1.51	1.02	1.00	2.20	0.88	1.43	0.95	1.75	0.89	0.54	0.47	0.67	1000	
methylene chloride	0.49		2.20	2.13	0.99	0.92	1.68	0.91	2.15	1.56	1.71	0.82			0.85	370	0.85
methyl iodide	1.34	5.26	1.94	1.95	1.68		4.70	2.03	1.86	2.06	2.33	2.14	1.21	1.25	1.15	870	1.06
nitromethane			41.0	38.5					39.5	10.4					4.41		
methanol			80	78.0	10.4	6.07		8.35	80						23.1		
carbon disulfide	2.66		1.30	1.33	2.63	5.03	15.1	4.03	1.26	1.75	3.20	5.51			1.27	3300	1.07
acetonitrile			30	31.5	1.73				31.3	7.48			1.80	2.14	4.00		5.05
1,2-dichloroethane			3.30		1.09				2.90		1.72		0.83	0.92		660	
ethyl bromide	1.04	4.19	1.62	1.63	1.50	1.70	3.56	1.53	1.62	1.99	2.05	1.73	1.09	1.27	0.98	970	1.00
ethyl iodide	1.55	6.17	1.90	1.87	1.83	2.79	6.16	2.22	1.80	2.29	2.40	2.68	1.35	1.55	1.06	2200	1.03
nitroethane			19.8	18.9					19.1								
ethanol			51	46.0	10.7	6.73		8.42	50.5						18.4		
propionitrile			21.9	20.0					20.9	6.34		0.96			2.64		
acetone	1.13	2.38		7.15	1.24				7.3	2.57			1.31	1.5	1.98		2.13
n-propyl chloride	1.10		1.47	1.47	1.81	1.90	4.44	1.64	1.47		2.68	1.87	1.29	1.59	1.05	3500	1.03
tetrahydrofuran				1.36					1.50								
butanone				3.86					4.15	2.02							
ethyl acetate			3.29	3.12	1.38				3.25	2.37		1.44	1.30	1.49	1.28		1.33
tert-butyl chloride	1.21		1.44		2.41	2.32	5.55					2.37	1.73	2.39	1.19	5300	1.24
isoprene	1.33		1.03	0.98	2.40	2.53	6.71	2.10	0.99	1.90		2.57	1.70	2.43	1.18		1.03
cyclopentadiene													2.26	2.81			
1-pentene	2.05		0.98	0.99	4.49	5.20		3.67	0.96			4.57			1.44		1.24
isopentene	2.05		0.97	0.97	3.72	5.00		3.41	0.94			4.51			1.37		1.19
pentane	3.09	9.6	1.00	0.98	7.46	9.62		6.50	0.97		10.9	8.53			1.80		1.48
chlorobenzene																3000	
benzene					1.39	1.82	3.86					1.84	1.07	1.32	0.99	2500	0.99
cyclohexane	3.24		0.99		5.79	9.61	36.8	5.70			7.2	8.4	3.41	4.35	1.59		1.35
hexane	3.49	12.0	1.00		8.20	11.4	58.0	7.50			13.0	11.0	4.57	6.50	1.74		1.44
isopropyl ether													2.51	3.14			
triethylamine	2.43				4.05		12.8					4.40			1.21		1.08
toluene											2.62					4500	
methylcyclohexane					7.22			6.8			10.2						
heptane					9.40			8.81			15.4						
isooctane					11.8												

[a] Solvent designations, column temperatures, types of packing, and means of determining solvent loadings are given in Table I.

the gas phase. A gas with a high heat-transfer coefficient such as helium will have its ability to transfer heat greatly reduced by the presence of foreign substances, so presaturation and stripping of solvent introduce impurities into the carrier gas and thus reduce the sensitivity of the detector. This means that many solutes cannot be detected in certain volatile solvents and represents the primary defect of the method. Use of a flame ionization detector is inapplicable to volatile solvents as the presence of solvent molecules would completely swamp the detector.

Theory

The equation used in calculating γ^∞ is

$$\gamma_2^\infty = \frac{RT\phi_2 Z_\mathrm{m} \exp(-V_2^\infty P/RT) n_1^{1}}{\phi_2^\mathrm{s} P_2^\mathrm{s} (V_\mathrm{R} - V_\mathrm{m})} \qquad (1)$$

where all the terms are defined at the end of the paper. This relation assumes that equilibrium is achieved throughout the column, that the solute is sufficiently dilute to be within the Henry's law region, and that the packing is inert relative to the solvent and the solute. The validity of these assumptions is discussed by Newman (*22*) and others (*23*, *31*–*33*) although further attention has recently been focused on the inertness problem of the packing (*23*–*27*, *31*–*37*).

Apparatus

The experimental apparatus was essentially that described earlier (*1*). Basically a controlled inert gas stream (helium) was presaturated with the volatile solvent and split, with half going to the reference side of a thermal conductivity detector and half going through the injection block and the test column. The entire system was thermostated to ±0.001 °C with a water bath, and elution times were read from a millivolt recorder. Gas flow rates were measured volumetrically by a soap bubble flowmeter.

Materials

Solvent purity is essential in the accurate measurement of limiting activity coefficients by chromatography. Purity of the solutes is not critical as the chromatograph separates impurities. Solvents were taken from sealed bottles of reagent quality (99% or better), and many were subjected to further purification. Refractive indices, when measured, were done so with a Bausch and Lomb refractometer on the Na 589 line. The solvent was considered pure when the deviation from the standard value was less than 0.0010 absolute. All solvents used in this study met that criterion with most deviations less than 0.0003. When appreciable water was suspected, the solvents were further purified by drying over molecular sieves or a drying agent such as calcium chloride and then distilled. The solvent manufacturers and purification procedures, if any, are included in Table I.

Procedure

The method of coating the substrate was essentially that of Parcher and Urone (*38*). The two different types of packing used were Fluoropack 80 (a Teflon substrate), produced by Applied Science Laboratories and Varian Aerograph, and Chrom W AW-DMCS, which was produced by Varian Aerograph and Johns-Manville. It was found that, if the weight of solvent within the column exceeded 1.5% the weight of the substrate for the Fluoropack and 15% for the Chrom W, then reproducible results (±10%) could be obtained for all detectable solutes. The Chrom W packing was first dried in a vacuum oven over 100 °C for 2–3 h. This step was skipped with the Teflon substrate as the particles aggregated below 100 °C. The packing was then mixed with solvent and allowed to stand in a refrigerator for several hours. For nonvolatile solvents, acetone was added to aid in wetting the packing.

Table III. Activity Coefficients at Infinite Dilution at 20 °C in Cyclohexanone[a]

	Teflon	Teflon	Teflon	Chrom W	Chrom W
tert-butyl chloride		1.31		1.31	1.32
n-propyl chloride		1.07		1.07	1.07
iodoethane	1.12	1.13		1.14	1.11
ethyl bromide		0.96		0.96	0.96
iodomethane		1.04	1.04	1.06	1.05
acetone		1.26		1.26	
methylene chloride	0.39	0.40		0.39	
acetonitrile	1.42	1.43			
n-hexane		4.24	4.46	4.54	4.53
cyclohexane		3.08		3.10	3.10
isoprene			1.43		1.48
carbon disulfide		1.86	1.88	1.86	1.85
carbon tetrachloride	1.10	1.10			1.10
benzene	0.93				
triethylamine	2.48	2.59			
n-pentane		3.89	4.00		
1-pentene		2.59			
isopentene		2.43	2.42		
% loading[b]	1.9	8.2	26	13	16

[a] Solvent loading determined by weighing and drying the substrate. [b] % loading = 100(weight of solvent)/(weight of substrate) for all solvents of this investigation.

The slurry was then transferred to a fluidizer similar to that used by Kruppa et al. (*39*). Excess liquid was drawn off by the house vacuum. The remaining liquid and substrate were then dried with N_2 until the acetone had evaporated and an amount of solvent remained on the packing that gave solvent loadings greater than 10% but small enough so that a solute could elute from the column in less than 30 min.

The packing was then loaded into a 0.25-in. copper tube with the help of a vibrator and a funnel. The ends of the tube were plugged with steel wool, and then the tube was bent into the shape of a U and connected to the chromatograph with Swagelock fittings.

Start-up consisted of allowing the helium to flow through the column for about 20 min, then turning the current to the filaments to 175 mA, and allowing the detector to equilibrate then for about 30 min. The flow rate through the test column was kept about 20 cm^3/min as Harris (*40*) stated is most efficient. The flow rates were checked frequently with a soap bubble meter and found to be quite constant. Upon equilibrium, 5-μL injections of air were made to determine the time required for an inert material to pass through the column. The retention time of air was then substracted from the other retention values. Roughly 0.15–0.35-μL injections of the solutes were then made sequentially. It was found that both polar and nonpolar molecules showed retention times independent of solute volumes below 0.2 μL when sufficient solvent coated the substrate. Injections above 0.2 μL (about 1% of the data) were made only when the solute could not be detected otherwise. The effect of this larger volume on the results was significantly less than the experimental uncertainty (*22*). The same solute was injected at the beginning and the end of each series of injections to check and account for stripping.

The determination of percent loading was the last step to be completed when Chrom W was the column substrate. Low Teflon aggregation temperatures prevented this step otherwise. To minimize the loss of solvent, we removed the column from the chromatograph as quickly as possible after the last sample was eluted and plastic tape was applied to both ends. The

Table IV. Comparison of the Limiting Activity Coefficients of This Study with Those in the Literature

		this work		literature			
solute	solvent	T, °C	γ^∞	T, °C	γ^∞	method[a]	ref
ethyl acetate	acetonitrile	20	1.58	40	1.53	ext	52
isoprene		20	6.03	20	6.35	GC	53
benzene		20	3.19	25	3.08	LLC	54
triethylamine		20	11.1	25	10.7	GC	55
ethanol	acetophenone	20	3.62	25	2.55	GC	49
isoprene		20	1.92	25	2.03	GC	17
isopentene		20	2.82	25	3.06	GC	17
pentane		20	6.00	25	5.37	GC	17
hexane		20	6.84	25	6.74	GS	45
heptane		20	7.58	25	6.82	GC	17
methanol	aniline	20	2.39	20	2.39	ext	56
acetone		20	0.80	40	0.87	ext	56
isoprene		20	5.27	25	4.90	GC	17
isopentene		20	8.61	25	9.00	GC	17
pentane		20	20.1	25	18.4	GC	17
hexane		20	25.7	25	26.63	GC	45
cyclohexane		20	13.6	25	11.9	GC	17
CCl$_4$	benzene	20	1.13	80	1.11	ext	46
chloroform		20	0.81	80	0.85	ext	46
methyl iodide		20	1.15	35	1.12	ext	46
CS$_2$		20	1.48	25	1.37	ext	46
acetonitrile		20	3.47	20	3.31	ext	46
acetone		20	1.71	59	1.63	EB	20
hexane		20	2.21	25	2.13	ext	46
hexane	benzonitrile	20	6.68	30	5.90	GC	57
cyclohexane		20	4.92	30	4.41	GC	57
hexane	benzyl acetate	20	5.28	30	4.11	GC	57
cyclohexane		20	3.45	30	3.12	GC	57
acetone	butanol	20	2.4	25	2.58	ext	50
cyclohexane		20	4.01	25	3.74	GC	17
pentane	butanone	20	3.66	25	3.65	ext	50
triethylamine		20	2.79	25	2.74	GC	55
acetonitrile	CCl$_4$	20	13.4	42	10.7	EB	20
cyclohexane		20	1.12	45	1.11	EB	20
nitromethane		20	15.2	45	11.7	EB	20
benzene		20	1.10	45	1.10	EB	20
cyclohexane	cyclohexanone	20	3.08	45	2.58	ext	46
isoprene		20	1.48	25	1.34	GC	58
acetone	1,2-dichloroethane	20	0.76	45	0.76	EB	20
hexane		20	5.04	31	4.40	EB	20
triethylamine	dimethylformamide	20	2.14	25	2.14	GC	55
isoprene		20	2.98	24	3.43	GC	16
1-pentene		20	8.00	24	7.30	GC	16
isopentene		20	6.67	24	6.86	GC	16
pentane		20	16.7	24	15.0	GC	16
hexane		20	20.8	25	17.9	GS	45
CCl$_4$	ethyl acetate	20	1.31	46	1.28	EB	20
triethylamine		20	2.43	25	2.46	GC	55
pentane	ethanol	20	9.6	25	9.0	ext	50
CCl$_4$	heptane	20	1.20	40	1.10	ext	46
chloroform		20	1.47	25	1.54	ext	46
acetonitrile		20	30.0	25	32.0	ext	46
ethyl iodide		20	1.90	30	2.03	ext	46
methanol		20	80.0	25	92.6	ext	50
ethanol		20	51.0	25	49.0	ext	50
ethanol	isooctane	20	46.0	40	27.0	ext	46
nitromethane		20	38.5	25	28.4	GC	49
isoprene	nitrobenzene	20	2.40	25	2.40	GC	17
hexane		20	8.20	25	7.81	GC	17
hexane	nitroethane	20	10.1	25	9.08	ext	46
acetone	octanol	20	2.57	25	2.58	ext	50
nitromethane		20	10.4	25	8.52	GC	49
pentane	phenol	50	10.9	50	11.3	ext	50
hexane		50	13.0	34	14.2	GC	17
cyclohexane		50	7.2	34	8.19	GC	17
toluene		50	2.62	50	3.3	ext	50
dichloromethane	water	20	370	20	209	GC	59
chloroform		20	1000	20	571	GC	59
CCl$_4$		20	6300	20	2870	GC	59
		20	4500	12.5	7100	ext	60

[a] ext = extrapolated VLE, GC = gas chromatographic, EB = ebulliometric, LLC = liquid-liquid chromatography, GS = gas stripping.

column was then rapidly dried and weighed. The contents of the column were emptied into an 18-mm diameter medium sintered glass filter of known weight after which the evacuated column was also weighed. The substrate in the filter was washed with acetone to a volume of 500 mm, dried in an oven at a temperature well above the boiling point of solvent for approximately 4 h, cooled, and weighed. The amount of substrate within the column and the weight of solvent upon the substrate were then calculated.

A more detailed description of the apparatus and procedure are available in ref *1*.

Data Reduction

Limiting activity coefficients may be calculated solely from experimental data and eq 1; however, the measurement of the moles of solvent loading on the column is subject to experimental error, especially for volatile solvents. Therefore, known γ^∞ values were used with eq 1 to calculate the amount of solvent within the column whenever possible. These known values came from a number of sources: other experimenters using the same technique, ebulliometric measurements or extrapolated VLE data. Obviously, if the standard value were found incorrect, the rest of the values would be off by the same relative amount.

Presentation of Results

The γ^∞'s of various solutes in 34 solvents are presented in Table II. The data are valuable as they represent many industrially interesting systems covering wide ranges of polarizability, polarity, and hydrogen-bonding ability. In addition, they are useful in determining parameters for the various predictive models (UNIFAC (*41*), ASOG (*42*), MSCED (*43*)). In Table I the solvent designations, column temperatures, types of packing, methods by which the solvent loadings were determined, and purification procedures are given for each solvent. Internal verifications of solvent loading by different methods check within experimental error. For cyclohexanone Table III demonstrates the reproducibility of the data for the two packings at different loadings. Table IV compares the values obtained here with those of other researchers. Further examples are shown elsewhere (*1*).

While the data are generally self-consistent to within 5%, their absolute accuracy is difficult to determine. The accuracy of the standard is probably better than 10% except possibly for water and benzyl chloride. The standard in benzyl chloride was chosen on the basis of data in related compounds (toluene and chlorobenzene) but the γ^∞ values of saturated hydrocarbons were much larger than anticipated. The standard in water, benzene, was obtained from the data of Duhem (*44*), but his method may not be valid for high activity coefficients. The chromatographic technique used here probably is not accurate to better than 40% for γ^∞'s greater than 100 and hence the data in water should be used with discretion. For the rest of the solvents, accuracy to 15% or better (barring a poor choice of standard) should be expected.

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Glossary

n_1^1	moles of solvent on the column
P	total pressure
P_2^s	saturation vapor pressure of solute
R	gas constant
T	temperature
V_R	retention volume of solute
V_m	volume of the mobile phase
V_2^∞	molar volume of solute at infinite dilution
Z_m	compressibility of the mixture
γ_2^∞	limiting activity coefficient of solute (2) in solvent (1)
ϕ_2	vapor-phase fugacity coefficient of solute at P
ϕ_2^s	fugacity coefficient of solute at P^s

Literature Cited

(1) Eckert, C. A.; Newman, B. A.; Nicolaides, G. L.; Long, T. C. *AIChE J.* **1981**, *27*, 33.
(2) Schreiber, L. B.; Eckert, C. A. *Ind. Eng. Chem. Process Des. Dev.* **1971**, *10*, 572.
(3) Tassios, D. *AIChE J.* **1971**, *17*, 1367.
(4) Smith, J. M.; VanNess, H. C. "Introduction to Chemical Engineering Thermodynamics"; McGraw-Hill: New York, 1975.
(5) Wong, K. F.; Eckert, C. A. *Ind. Eng. Chem. Fundam.* **1971**, *10*, 20.
(6) Porter, P. E.; Deal, C. H.; Strauss, F. H. *J. Am. Chem. Soc.* **1956**, *78*, 2999.
(7) Evered, S.; Pollard, F. H. *J. Chromatogr.* **1960**, *4*, 451.
(8) Kwantes, A.; Rijnders, G. W. A. "*Gas Chromatography*"; Buttersworth: London, 1958 and references cited therein.
(9) Everett, D. H.; Stoddart, C. T. H. *Trans. Faraday Soc.* **1961**, *57*, 746.
(10) James, A. T.; Martin, A. J. P. *Biochem. J.* **1952**, 679.
(11) Ashworth, A. J.; Everett, D. H. *Trans. Faraday Soc.* **1960**, *56*, 1609.
(12) Littlewood, A. B. *Anal. Chem.* **1964**, *36*, 1441.
(13) Littlewood, A. B.; Willmott, F. W. *Anal. Chem.* **1966**, *38*, 1031.
(14) Parcher, J. F.; Weiner, P. H.; Hussey, C. L.; Westlake, T. N. *J. Chem. Eng. Data* **1975**, *20*, 145.
(15) Comanita, V. J.; Greenkorn, R. A.; Chao, K. *J. Chem. Eng. Data* **1976**, *21*, 491.
(16) Smiley, H. M. *J. Chem. Eng. Data* **1970**, *15*, 413.
(17) Vernier, P.; Raimbault, C.; Renon, H. *J. Chim. Phys. Phys.-Chim. Biol.* **1969**, *66*, 429.
(18) Harris, H. G.; Prausnitz, J. M. *J. Chromatogr. Sci.* **1969**, *7*, 685.
(19) Laub, R. J.; Martire, D. E.; Purnell, J. H. *J. Chem. Soc., Faraday Trans. 2* **1978**, *74*, 213.
(20) Thomas, E. R.; Newman, B. A.; Nicolaides, G. L.; Eckert, C. A. *J. Chem. Eng. Data*, in press.
(21) Martire, D. E., Pecsok, R. L.; Purnell, J. H. *Nature (London)* **1964**, *203*, 1279.
(22) Newman, B. A. Ph.D. Dissertation, University of Illinois, Urbana, IL 1977.
(23) Berezkin, V. G. *J. Chromatogr.* **1978**, *159*, 359.
(24) Martire, D. E.; Pollara, L. Z. *Adv. Chromatogr.* **1951**, *1*, 335.
(25) Boheman, J.; Langer, S. H.; Perret, R. H.; Purnell, J. H. *J. Chem. Soc.* **1960**, 2444.
(26) Zhukhovitskii, A. A.; Berezkin, V. G.; Lunskii, M. Kh.; Burova, M. G.; Khobotova, T. P. *J. Chromatogr.* **1975**, *104*, 241.
(27) Veening, H.; Huber, J. F. K. *J. Gas Chromatogr.* **1968**, *6*, 326.
(28) Everett, D. H.; Gainey, B. W.; Young, C. L. *Trans. Faraday Soc.* **1968**, *64*, 2667.
(29) Cruickshank, A. J. B.; Gainey, B. W.; Young, C. L. *Trans. Faraday Soc.* **1968**, *64*, 337.
(30) Desty, D. H.; Swanton, W. T. *J. Phys. Chem.* **1961**, *65*, 766.
(31) Martin, R. L. *Anal. Chem.* **1961**, *33*, 347.
(32) Locke, D. C. *Adv. Chromatogr.* **1976**, *14*, 87.
(33) Mathiasson, L.; Jönsson, J. A. *J. Chromatogr.* **1979**, *179*, 7.
(34) Serpinet, J. *Anal. Chem.* **1976**, *48*, 2264.
(35) Conder, J. R. *Anal. Chem.* **1976**, *48*, 917.
(36) Conder, J. R., Locke, D. C.; Purnell, J. H. *J. Phys. Chem.* **1969**, *73*, 700.
(37) Conder, J. R. *J. Chromatogr.* **1969**, *39*, 237.
(38) Parcher, J. F.; Urone, P. J. *J. Gas Chromatogr.* **1964**, *2*, 184.
(39) Kruppa, R. F.; Henly, R. S.; Smead, D. L. *Anal. Chem.* **1967**, *39*, 851.
(40) Harris, H. G. Ph.D. Dissertation, University of California, Berkeley, CA, 1968.
(41) Fredenslund, A.; Gmehling, J.; Rasmussen, P. "Vapor-Liquid Equilibria Using UNIFAC"; Elsevier: New York, 1977.
(42) Kojima, K.; Tochigi, K. "Predictions of Vapor-Liquid Equilibria by the ASOG Method"; Elsevier: New York, 1979.
(43) Thomas, E. R.; Eckert, C. A. *Ind. Eng. Chem. Process Des. Dev.*, submitted for publication.
(44) Duhem, P.; Vidal, J. *Fluid Phase Equilib.* **1978**, *2*, 231.
(45) Leroi, J.-C.; Masson, J.-C.; Renon, H.; Fabries, J.-F.; Sannier, H. *Ind. Eng. Chem. Process Des. Dev.* **1977**, *16*, 139.
(46) Gmehling, J.; Onker, U. "Vapor-Liquid Equilibrium Data Collection"; Chemistry Data Series, DECHEMA (Deutsche Gesellschaft für Chemisches Apparatewesen): Frankfurt, West Germany, 1977–1980; Vol. 1, Part 107.
(47) Galle, A. A.; Parizheval, N. V.; Proskuryakov, V. A. *Zh. Prikl. Khim. (Leningrad)* **1974**, *47*, 191.
(48) Marsh, K. N.; French, H. T.; Roger, H. P. *J. Chem. Thermodyn.* **1979**, *11*, 897.
(49) Rohrschneider, L. *Anal. Chem.* **1973**, *45*, 1241.
(50) Deal, C. H.; Derr, E. L. *Ind. Eng. Chem. Process Des. Dev.* **1964**, *3*, 394.
(51) Gerster, J. A.; John, A.; Gorton, E. J. *J. Chem. Eng. Data* **1960**, *5*, 423.
(52) Muthu, O.; Maher, P. H.; Smith, D. B. *J. Chem. Eng. Data* **1980**, *25*, 163.
(53) Breban, D.; Gothard, F. A. *Rev. Chim. (Bucharest)* **1972**, *23*, 749.
(54) Locke, D. C. *Adv. Chromatogr.* **1969**, *8*, 47.

J. Chem. Eng. Data **1982**, *27*, 405–412

(55) Abraham, M. H.; Greller, P. L.; Mana, J. *J. Chem. Thermodyn.* **1974**, *6*, 1175.
(56) Maher, P. J.; Smith, B. D. *J. Chem. Eng. Data* **1980**, *25*, 61.
(57) Pul'tsin, M. N.; Galle, A. A.; Proskuryakov, V. A. *Russ. J. Phys. Chem.* (*Engl. Transl.*) **1973**, *47*, 428.
(58) Monfort, J. P.; Vidal, J.; Renon, H. *J. Chim. Phys. Phys.-Chim. Biol.* **1970**, *67*, 748.
(59) Pecsar, R. E.; Martin, J. J. *Anal. Chem.* **1966**, *38*, 1661.
(60) Karger, B. L.; Sewell, P. A.; Castells, R. C.; Hartkopf, A. *J. Colloid Interface Sci.* **1971**, *35*, 328.

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Vapor Pressures of Some C_4 Hydrocarbons and Their Mixtures

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New experimental vapor pressures for the six binary systems containing 1,3-butadiene, *n*-butane, *trans*-2-butene, and *cis*-2-butene at temperatures from 278 to 358 K are reported. Relative volatilities were calculated by using the isothermal general coexistence equation.

Recent investigators (*1*, *2*) have demonstrated the utility of the total pressure technique for obtaining vapor–liquid equilibrium information on systems of close-boiling components of sufficient accuracy to be used in distillation design. Laurance and Swift (*3*), Steele et al. (*4*), and Martinez-Ortiz and Manley (*5*), in particular, have presented vapor pressures for various combinations of the C_4 hydrocarbon isomers. This study is a continuation and extension of their work. Vapor pressures were measured for 1,3-butadiene, *n*-butane, *trans*-2-butene, *cis*-2-butene, and the six binary combinations of these four isomers. Temperature ranges were 278–338 K for butadiene and mixtures containing butadiene and 278–358 K for the remaining isomers and their mixtures.

Theory

The isothermal Gibbs–Duhem equation for a two-component system is

$$(V\,dP)/RT = z_1\,d\ln f_1 + z_2\,d\ln f_2 \tag{1}$$

Writing this equation for both vapor and liquid phases and subtracting, noting that $f_i^V = f_i^L$ at equilibrium, gives

$$(1/RT)(V^V - V^L)\,dP = (y_1 - x_1)\,d\ln f_1 + (y_2 - x_2)\,d\ln f_2 \tag{2}$$

or

$$(1/RT)(V^V - V^L)\,dP = (y_1 - x_1)\,d\ln(f_1/f_2) \tag{3}$$

The fugacities are given by

$$f_i = y_i\phi_i P \tag{4}$$

At this point it is necessary to decide upon an equation of state for the vapor phase in order to calculate the fugacity coefficient, ϕ_i. The virial equation truncated after the second term was judged to be sufficient for these systems. The Berlin form

$$Z = V^V P/RT = 1 + BP \tag{5}$$

is somewhat more convenient to use than the Leiden form. The mixture virial coefficient, B, is taken to be

$$B = y_1B_1 + (1 - y_1)B_2 \tag{6}$$

Using the commonly known relationship between fugacity and an equation of state

$$\phi_i = \exp(B_i P) \tag{7}$$

It is further assumed that the liquid phase forms an ideal mixture

$$V^L = x_1V_1^L + (1 - x_1)V_2^L \tag{8}$$

where V_i^L is the saturated-liquid volume. We are interested in calculating relative volatilities, so y_1 in the above equations will be replaced by α according to the relation

$$\alpha = y_1(1 - x_1)/[(1 - y_1)x_1] \tag{9}$$

Combining eq 3–9 gives the result

$$\frac{(\alpha - 1)(1 - x)x}{1 + (\alpha - 1)x}\,\frac{d\ln\alpha}{dx} + \frac{\alpha - 1}{1 + (\alpha - 1)x} = A\,\frac{d\ln P}{dx} \tag{10}$$

$$A = \text{fcn}\,(x,P;V_1^L,B_i) \tag{11}$$

where x is for the first component. Equation 10 is then integrated for α using the experimentally determined $P - x$ function.

Experimental Section

The equipment of Walker (*6*) and Steele (*7*) was used with only slight modifications to improve the reliability and speed. The primary element is an enclosed equilibrium cell immersed in a thermostated water bath. By means of a diaphragm mechanism, the pressure within the cell was balanced against an external nitrogen pressure which was then measured. The system was capable of handling up to four equilibrium cells at a time which significantly decreased the amount of time required to complete a binary. The temperature of the water bath was measured with a Leeds and Northrup platinum resistance thermometer calibrated by the National Bureau of Standards to the IPTS of 1968. Pressures at 278 K were measured with a Mensor Corp. quartz manometer, and those at the upper temperature with a Ruska Corp. dead-weight gauge with calibration traceable to NBS.

Phillips research-grade hydrocarbons were used which had stated purities of not less than 99.95, 99.95, 99.80, and 99.97 wt % for butadiene, *n*-butane, *trans*-2-butene, and *cis*-2-butene, respectively. Noncondensables were removed by a freezing and evacuating cycle. Analysis of the vapor phase by gas chromatograph showed no detectable noncondensable. The chromatograph was capable of detecting air mole fractions

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