

- (5) Goodwin, R. D., *Natl. Bur. Stand. (U.S.), Tech. Note*, 653 (1974).
 (6) Jacobsen, R. T., Stewart, R. B., *Natl. Bur. Stand. (U.S.), Tech. Note*, 648 (1973).
 (7) McGlashan, M. L., Wormald, C. J., *Trans. Faraday Soc.*, **60**, 646 (1964).
 (8) Pitzer, K. S., Curl, R. F., *J. Am. Chem. Soc.*, **79**, 2369 (1957).
 (9) Prausnitz, J. M., "Molecular Thermodynamics of Fluid-Phase Equilibrium", Prentice-Hall, Englewood Cliffs, N.J., 1968, Chapter 5.

- (10) Rigby, M., Prausnitz, J. M., *J. Phys. Chem.*, **72**, 330 (1968).
 (11) Tremper, K. K., Prausnitz, J. M., *J. Chem. Eng. Data*, **21**, 295 (1976).

Received for review March 15, 1976. Accepted July 29, 1976. For financial support, the authors are grateful to the American Petroleum Institute, the National Science Foundation, the American Gas Association, and the donors of the Petroleum Research Fund, administered by the American Chemical Society.

Activity Coefficients at Infinite Dilution: Alcohols and Esters in *n*-Hexadecane, Alcohols in Ethyl Octanoate, and Esters in 1-Octadecanol

V. John Comanita, Robert A. Greenkorn, and Kwang-Chu Chao*

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

Gas-liquid partition chromatography was used to determine infinite dilution activity coefficients in binary liquid solutions at 100–140 °C. The binary systems studied are: alcohols and esters in *n*-hexadecane, alcohols in ethyl octanoate, and esters in 1-octadecanol.

Infinite dilution activity coefficients in binary solutions are important quantities in solution thermodynamics. They define useful boundary conditions in the integration of the Gibbs–Duhem equation, and are therefore valuable for the description of the solution behavior of the entire binary solution system. Schreiber and Eckert (5) showed that the Wilson equation gives consistently reliable results when the equation constants are determined from infinite dilution activity coefficients and the same results hold when the equation is extended to multicomponent systems.

In this work we determine the infinite dilution activity coefficients in a number of systems: methanol, ethanol, propanol, and 1-butanol in *n*-hexadecane and in ethyl octanoate; methyl acetate, methyl propionate, and ethyl propionate in *n*-hexadecane and in 1-octadecanol. The molecules studied contain structural groups of wide interest. We are interested in determining the interaction properties of these groups from analysis of these and other data. Meanwhile the present data can be of direct interest for the description of the behavior of the binary solutions studied.

The gas-liquid partition chromatograph and experimental procedure that we used in this work have been described (1, 6). Retention time was determined as the elapsed time required by the injected solute to travel through the chromatograph column in which the packing was loaded with the solvent. The solute was carried by the helium elution gas through a conductivity cell both before and after passing through the chromatograph column. The time of the conductivity cell output peak was recorded as a digital signal accurate to 0.1 s. The equilibrium vaporization ratio *K* of the solute was obtained from the retention time and was found to be reproducible to about 3%.

The column temperature is controlled to within ±0.25 °C, pressure to ±0.02 atm, and flow rate to 2%. Detailed error analysis of the contributing factors showed the uncertainty of the measured *K* values to be about 3% in agreement with the directly observed uncertainty.

K values were obtained from the direct experimental observables by

$$K_i = \frac{nz_a}{p_a F_a} \frac{RT_a}{(t_{Ri} - t_g)} \quad (1)$$

The equation has been described (6). The symbols are explained in the glossary section. *K* values were determined at four pressures for each temperature. Figure 1 illustrates the results with propanol in *n*-hexadecane.

From plots like Figure 1 interpolation was made to obtain *K* values at a conveniently low pressure, fixed at 1.7 atm in this

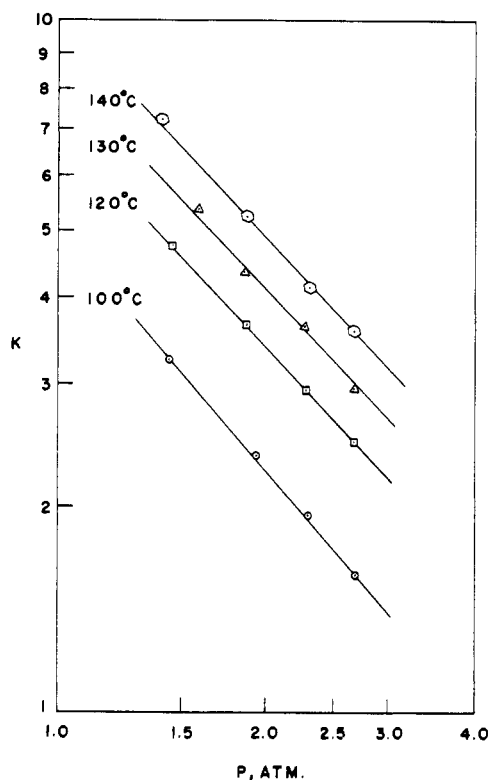


Figure 1. *K* values of propanol at infinite dilution in He-*n*-hexadecane.

Table I. *K* Values, Vapor Pressures, Fugacity Coefficients, and Infinite Dilution Activity Coefficients of Alcohols in *n*-Hexadecane at 1.70 atm

	<i>K</i>	<i>p</i> ⁰ , atm	<i>φ</i> ⁰	<i>γ</i> [∞]	<i>K</i>	<i>p</i> ⁰ , atm	<i>φ</i> ⁰	<i>γ</i> [∞]
	100 °C				120 °C			
Methanol	16.40	3.452	0.941	8.59	21.60	6.255	0.919	6.39
Ethanol	7.10	2.228	0.949	5.71	10.10	4.243	0.927	4.37
Propanol	2.70	1.100	0.966	4.32	4.00	2.208	0.950	3.24
1-Butanol	1.15	0.53	0.976	3.77	1.78	1.08	0.965	2.90
	130 °C				140 °C			
Methanol	24.60	8.213	0.906	5.62	27.20	10.630	0.890	4.89
Ethanol	11.60	5.685	0.913	3.80	13.00	7.486	0.897	3.29
Propanol	4.85	3.022	0.940	2.90	5.70	4.055	0.978	2.58
1-Butanol	2.20	1.50	0.959	2.60	2.65	2.05	0.951	2.30

Table II. *K*-Values, Vapor Pressures, Fugacity Coefficients, and Infinite Dilution Activity Coefficients of Alcohols in Ethyl Octanoate at 1.70 atm

	110 °C				120 °C				130 °C			
	<i>K</i>	<i>p</i> ⁰ , atm	<i>φ</i> ⁰	<i>γ</i> [∞]	<i>K</i>	<i>p</i> ⁰ , atm	<i>φ</i> ⁰	<i>γ</i> [∞]	<i>K</i>	<i>p</i> ⁰ , atm	<i>φ</i> ⁰	<i>γ</i> [∞]
Methanol	6.40	4.688	0.929	2.50	7.35	6.255	0.919	2.17	8.50	8.213	0.906	1.94
Ethanol	3.43	3.107	0.937	2.00	4.00	4.243	0.927	1.73	4.68	5.685	0.913	1.53
Propanol	1.43	1.577	0.959	1.61	1.70	2.208	0.950	1.38	1.98	3.022	0.940	1.19
1-Butanol	0.60	0.73	0.971	1.44	0.76	1.08	0.965	1.24	0.94	1.50	0.959	1.11

Table III. *K* Values, Vapor Pressures, Fugacity Coefficients, and Infinite Dilution Activity Coefficients of Esters in *n*-Hexadecane at 1.70 atm

	<i>K</i>	<i>p</i> ⁰ , atm	<i>φ</i> ⁰	<i>γ</i> [∞]	<i>K</i>	<i>p</i> ⁰ , atm	<i>φ</i> ⁰	<i>γ</i> [∞]
	100 °C				120 °C			
Methyl acetate	3.42	3.66	0.93	1.71	5.02	5.98	0.89	1.60
Methyl propionate	1.54	1.85	0.95	1.49	2.37	3.16	0.920	1.39
Ethyl propionate	0.825	0.99	1.00	1.41	1.32	1.83	0.950	1.29
	130 °C				140 °C			
Methyl acetate	6.00	7.53	0.87	1.56	7.05	9.33	0.85	1.51
Methyl propionate	2.88	4.00	0.905	1.35	3.52	5.11	0.89	1.31
Ethyl propionate	1.65	2.40	0.935	1.25	2.03	3.08	0.92	1.21

Table IV. *K* Values, Vapor Pressures, Fugacity Coefficients, and Infinite Dilution Activity Coefficients of Esters in 1-Octadecanol at 1.70 atm

	110 °C				120 °C				130 °C			
	<i>K</i>	<i>p</i> ⁰ , atm	<i>φ</i> ⁰	<i>γ</i> [∞]	<i>K</i>	<i>p</i> ⁰ , atm	<i>φ</i> ⁰	<i>γ</i> [∞]	<i>K</i>	<i>p</i> ⁰ , atm	<i>φ</i> ⁰	<i>γ</i> [∞]
Methyl acetate	3.45	4.72	0.91	1.37	4.08	5.98	0.89	1.30	4.80	7.53	0.87	1.25
Methyl propionate	1.62	2.48	0.935	1.19	1.97	3.16	0.920	1.15	2.35	4.00	0.905	1.10
Ethyl propionate	0.90	1.40	0.965	1.13	1.12	1.83	0.950	1.10	1.37	2.40	0.935	1.04

Table V. Sources and Purities of Chemicals

Chemical	Company	Purity
<i>n</i> -Hexadecane	Phillips	"pure" 99% min
Ethyl octanoate	Eastman	95% min, bp range 91–93 °C at 13 mm
1-Octadecanol	Eastman	95% min, mp range: 56.5–58 °C
Methanol	Baker	"Reagent" 99.95% min, bp range: 64.6–64.9 °C
Ethanol	Mallinckroft	Absolute anhydrous, 99.5% min
1-Propanol	Fisher	"Reagent" 99.95% min, bp range 96.8–97.5 °C
1-Butanol	Matheson Coleman & Bell	"Spectroquality" 99% min
Methyl acetate	Eastman	99.8% min, bp range 56.7–57.5 °C
Methyl propionate	Eastman	95% min, bp range 79–81 °C
Ethyl propionate	Eastman	Bp range 97–99 °C, 95% min

work, for calculating activity coefficient according to the equation

$$\gamma_i = \frac{p\phi_i K_i}{p_i^0 \phi_i \exp[(p - p_i^0) \bar{V}_i / RT]} \quad (2)$$

The equation has been described (1, 6). The activity coefficient was found to be independent of the pressure in the lower pressure range of the experiments where pK_i remains constant at a given temperature, and 1.7 atm is conveniently in this range.

Tables I through IV show the liquid phase activity coefficients along with the fugacity coefficients ϕ^0 and vapor pressures p^0 of the pure solutes used in their calculations. The fugacity coefficient ϕ of the solute vapor at infinite dilution in helium gas was also required in the calculations and was taken to be equal to 1. The ϕ^0 values of the esters were obtained from the generalized correlation by Lydersen, Greenkorn, and Hougen (4). The ϕ values of the alcohols were calculated based on second virial coefficient data compiled by Dymond and Smith (2). The vapor pressures were taken from Jordan's compilation (3), and extrapolated by means of a Cox chart where necessary.

The sources and purities of the chemicals used are shown in Table V.

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_{R_i}	retention time of solute i
t_g	retention time of hypothetical "nonabsorbed" gas

T	absolute temperature
T_a	absolute ambient temperature
V_i	liquid molal volume of component i
z_a	compressibility factor of elution gas at ambient conditions
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 at T and p_i^0

Literature Cited

- (1) Comanita, V. J., M.S. Thesis, Purdue University, West Lafayette, Ind., Dec 1975.
- (2) Dymond, J. H., Smith, E. B., "The Virial Coefficients of Gases", Clarendon Press, Oxford, 1969.
- (3) Jordan, T. E., "Vapor Pressure of Organic Compounds", Interscience, New York, N.Y., 1954.
- (4) Lydersen, A. L., Greenkorn, R. A., Hougen, O. A., "Generalized Thermodynamic Properties of Pure Fluids", Engineering Experiment Station Report No. 4, University of Wisconsin, Madison, Wis., 1955.
- (5) Schreiber, L. B., Eckert, C. A., *Ind. Eng. Chem. Process Des. Dev.*, **10**, 572 (1971).
- (6) Turek, E. A., Comanita, V. J., Greenkorn, R. A., Chao, K. C., *J. Chem. Eng. Data*, **21**, 209 (1976).

Received for review March 22, 1976. Accepted July 6, 1976. This work was supported by NSF Grant GK-42051.

Dew Point Study in the Vapor-Liquid Region of the Methane-Carbon Dioxide System

Shuen-Cheng Hwang, Ho-mu Lin,[†] Patsy S. Chappellear,^{*‡} and Riki Kobayashi*

Department of Chemical Engineering, William Marsh Rice University, Houston, Texas 77001

The elution technique has been used to study the vapor phase concentration along isotherms in the vapor-liquid region surrounding the vapor-solid region for the methane-carbon dioxide system. Temperatures from -65.00 to -184.00 °F were investigated. The pressure range covered from the three-phase solid-liquid-vapor locus to the critical point or the vapor pressure of methane. Several temperatures matched a previous study in another laboratory in the vapor-solid region. Measurements were intensified near the critical temperature of methane.

There has been a number of studies of the vapor-liquid equilibrium of the methane-carbon dioxide system. However, most of these studies were made at higher temperatures well above the critical temperature of methane, only one investigation included temperatures below the critical temperature of methane.

Both vapor and liquid phases were studied by Arai et al. (1) at 59, 32, and -4 °F; by Kaminishi et al. (6) at 50, 32, -4 , and -40 °F; and by Donnelly and Katz (4) at temperatures in the range 29 to -100 °F. Sterner (10) measured vapor-liquid equilibria at -90 , -95 , and -100 °F; however, no critical points

were determined. The only investigation which covered the temperature range below methane critical temperature was that by Neumann and Walch (7) over the range of -64 to -148 °F.

The solid-liquid-vapor phase behavior of the methane-carbon dioxide system was studied by Pikaar (8) and by Davis, Rodewald, and Kurata (3). These experimental results have been useful in this investigation for the determination of the triple-point vapor composition locus. The vapor-solid equilibria by Pikaar (8) are used for examining the transition between vapor-liquid and vapor-solid regions.

Equipment and Method

In the elution technique, the presaturator and the equilibrium cell are charged with the less volatile component, carbon dioxide in this case. The more volatile component is added to provide the desired system pressure and then eluted through the cell, with a partial recycle to hasten equilibrium. The concentration of the eluted stream is monitored until steady state is achieved.

The main equipment components which were used in the constant flow saturation method consisted of a 410 stainless-steel windowed cell with a pressure rating of 8000 psi, a cryostatic bath, a carrier gas metering pump, and analytic equipment. Extensive details of the equipment and method have been reported earlier (2).

The flow chart of the equipment layout is shown in Figure 1.

[†] Present address, School of Chemical Engineering, Purdue University, West Lafayette, Ind. 47907.

[‡] Address correspondence to this author at McDermott Hudson Engineering Corp., Houston, Texas 77036.