ACKNOWLEDGMENT

We thank W. S. MacGregor of the Crown Zellerbach Corp. for making available to us his literature survey on the refractive index of dimethylsulfoxide. We thank S. E. Wood of Illinois Institute of Technology and W. C. Mallard of Emory for suggesting use of the method of minimum deviation to us.

LITERATURE CITED

(1) Butler, R. D., *Amer. Mineral.*, **18**, 386 (1933).
(2) Fairbairn, H. W., *ibid.*, **37**, 37 (1952).
(3) Forziati, A. F., *J. Res. Nat. Bur. Stand.*, **44**, 373 (1950).
(4) Forziati, A. F., Camin, D. L., Rossini, F. D., *ibid.*, **45**, 406 (1950).
(5) Forziati, A. F., Glasgo, A. R., Jr., Willingham, C. B., Rossini, F. D., *ibid.*, **36**, 129 (1946).
(6) Forziati, A. F., Rossini, F. D., *ibid.*, **43**, 473 (1949).
(7) Gogswell, R. F., *Amer. Mineral.*, **30**, 541 (1945).
(8) Hafner, H. C., Rood, J. L., *Mater. Res. Bull.*, **2**, 303 (1967).
(9) Kenttamaa, J., Lindberg, J., *Suom. Kemistilehti*, **33B**, 32 (1960).
(10) Larsen, E. S., Berman, H., *U.S. Geol. Surv. Bull.*, 848, 2nd ed., 18–20 (1934).
(11) Patnode, W., Wilcock, D. F., *J. Amer. Chem. Soc.*, **68**, 358 (1946).
(12) Rossini, F. D., Pitzer, K. S., Taylor, W. J., Ebert, J. P., Kilpatrick, J. E., Beckett, C. W., Williams, M. G., Werner, H. G., *Selected Values of Properties of Hydrocarbons*, National Bureau of Standards Circ. C461, 1947.
(13) Schlafer, H. L., Schaffernicht, W., *Angew. Chem.*, **72**, 618 (1960).
(14) Tilton, L. W., *J. Res. Nat. Bur. Stand.*, **2**, 909 (1929).
(15) Tilton, L. W., *ibid.*, **6**, 59 (1931).
(16) Tilton, L. W., *ibid.*, **11**, 25 (1933).
(17) Tilton, L. W., *ibid.*, **14**, 393 (1935).
(18) Tilton, L. W., Taylor, J. K., *ibid.*, **20**, 419 (1938).
(19) Traynelis, V. J., Hergenrother, W. L., Livington, J. R., Valicenti, J. A., *J. Org. Chem.*, **27**, 2377 (1962).
(20) Traynelis, V. J., Hegenrother, W. L., Hanson, H. T., Valicenti, J. A., *ibid.*, **29**, 123 (1964).
(21) Wibaut, J. P., Hoog, H., Langedijk, S. L., Overhoff, J., Smittenberg, J., *Rec. Trav. Chim.*, **58**, 329 (1939).
(22) Wibaut, J. P., Langedijk, S. L., *ibid.*, **59**, 1220 (1940).
(23) Wolfe, C. W., Franklin, V., *Amer. Mineral.*, **34**, 893 (1949).
(24) Wood, R. W., "Physical Optics," Dover Publications, New York, N. Y., 1967, pp 75–77.

RECEIVED for review July 6, 1970. Accepted October 3, 1970. Investigation supported by research grant GO-8364 from the National Science Foundation. Presented at the Southeastern Regional Meeting, ACS, Richmond, Va., November 1969.

Solubility of Cyclopropane in Alkyl Carboxylic Acids

JAMES R. BARTON[1] and CHENG C. HSU[2]
Department of Chemical Engineering, Queen's University, Kingston, Ont., Canada

The solubility of cyclopropane gas in acetic, propionic, *n*-butyric, *i*-butyric, and *n*-valeric acids has been measured over the temperature range of 0–40° C at a partial gas pressure of one atmosphere. The experimental error is estimated to be within 0.5%. The results show that the solubility increases with increasing chain length in the homologous series.

Gas solubilities provide useful information for the study of highly nonideal liquids such as the carboxylic acids which tend to associate, by hydrogen bonding, to form dimers. The solubilities of several gases in acetic have been reported in the literature (*2*, *8*). Very few solubility data exist, however, for nonpolar gases in the other carboxylic acids.

In this work, an experimental investigation of the solubilities of nonpolar gases in several carboxylic acids has been made, employing an apparatus based on the original design of Markam and Kobe (*9*). The solubility of cyclopropane gas in acetic, propionic, *n*-butyric, *i*-butyric, and *n*-valeric acids has been measured over the temperature range of 0–40° C at a partial gas pressure of 1 atm. Reliable density data for these acids are also presented for the same temperature range.

The reliability of the equipment was checked by determination of the solubilities of carbon dioxide in water and cyclopropane in aliphatic alcohols.

EXPERIMENTAL

The Ostwald type of apparatus which was constructed for this study was based on the original design of Markam and Kobe (*9*), but also included the modifications suggested by Yen and McKetta (*14*). The measurement of the solubility of a gas in a liquid using this type of apparatus involves four main steps. A sample of the liquid solvent must be measured at a gas partial pressure of 1 atm. The saturated gas and liquid solvent are then mixed until an equilibrium quantity of the gas has dissolved at the temperature of the experiment. Finally, the volume of the saturated gas remaining, at a partial gas pressure of 1 atm, is determined. In actual operation, at least two equilibrium positions are determined at different partial pressures of gas; one above 760 mm Hg and one below. The equilibrium position at a partial pressure of 1 atm is then obtained by linear interpolation. The total pressure corresponding to the partial pressure of the solute is calculated from vapor pressure data by assuming ideal gas mixture.

The difference in the gas volumes before and after dissolution permits the calculation of the gas solubility in terms of the Bunsen coefficient which is defined as: "the volume of gas, reduced to 0° C and 760 mm Hg, which is absorbed by a unit volume of solvent, at the temperature of the measurement, under a partial gas pressure of 760 mm Hg."

The solubility in terms of mole fraction is easily calculated from the Bunsen coefficient.

The volume of the liquid solvent was determined by isolating it in a previously calibrated Pyrex bulb. The

---

[1] Present address, Research Center, Du Pont of Canada Ltd., Kingston, Ont., Canada

[2] To whom correspondence should be addressed.

volume of the bulb as a function of temperature was determined with less than 0.10% error. The gas volumes were determined by means of a buret fabricated from precision-bore Pyrex glass tubing. The mercury level in the buret was read with a cathetometer having a minimum division of 0.02 mm. The maximum error in determination of a gas volume is estimated to be ±0.05%. The gas buret serves also as the right leg of a manometer for measuring gas pressures in the system.

The temperature of the thermostatic bath is controlled by a Sargent Thermonitor model S-82052 temperature controller and is measured by an iron-constantan thermocouple in conjunction with K-3 potentiometer and type E galvanometer, both products of Leeds & Northrup Co. The thermocouple was calibrated against NBS certified thermometer. With this combination, the temperature could be easily measured to within 0.05° C.

A detailed description of the operating procedures is given elsewhere (*1*).

MATERIALS

The Coleman grade CO_2 employed in this work was obtained from the Matheson Co. and had a reported minimum purity of 99.99%. The cyclopropane gas was obtained from the Ohio Chemical Co. as USP grade with a minimum purity of 99.9%. They were used without further purification.

The distilled water employed in performance evaluation runs had a refractive index of 1.3332 at 19.5° C, in good agreement with a literature value of 1.3333 at the same temperature (*4*). All refractive indices reported in this work were measured with a Bausch and Lomb ABBE-3L refractometer. The isopropyl alcohol was Certified ACS spectroanalyzed grade with a water content of 0.10%. The refractive index of this alcohol was 1.3752, in good agreement with a reported value (*6*) of 1.37508, both measurements at 25° C. The methanol was spectrophotometer quality with a reported purity of 99.7%. The refractive index at 25° C was 1.3267, in agreement with a reported value (*6*) of 1.3266. The normal propanol was certified reagent grade and had a refractive index of 1.3834, which compares favorably with a reported value (*6*) of 1.3832, both at 25° C.

Physical data on the carboxylic acids used in this work are listed in Table I. As indicated by the vendors' specifications and confirmed by the refractive indices, the acetic and propionic acids are of very high purity. For valeric and butyric acids, the vendors' analyses do not give a direct indication of purity. However, a comparison of the refractive indices and densities of these acids with literature values suggests purities comparable to those listed for acetic and propionic acids.

RESULTS

Performance results on the apparatus with the system CO_2 in water are presented in Table II. These data are in excellent agreement with the reliable values reported in the literature. The estimated reproducibility of the apparatus of less than ±0.5% error is confirmed by the data for CO_2 in water.

Since the solubilities of cyclopropane in the carboxylic acids were expected to be very much greater than those of CO_2 in water, the reliability of the apparatus was further investigated by measuring the solubilities of cyclopropane in several alcohols. Such data have previously been reported by Loeffler and McKetta (*6*) and were expected to be

Table I. Source, Purity, and Refractive Index of Carboxylic Acids

		Vendor's specifications		Refractive index, 20° C	
Acid	Source	Grade	Reptd purity, %	This work	Literature
Acetic	Baker	Baker Analyzed Reagent	99.9	1.3720	1.3716 (*4*) 1.3718 (*11*) 1.3716 (*12*)
Propionic	Fisher	Certified	99.83	1.3872	1.3869 (*4*) 1.3874 (*11*) 1.3865 (*12*)
n-Butyric	Baker	Baker grade	99.0 Min	1.3986	1.3980 (*4*) 1.3990 (*11*) 1.3980 (*12*)
i-Butyric	Baker	Baker grade	. . .	1.3932	1.3930 (*4*) 1.3930 (*11*)
n-Valeric	Baker	Baker grade	. . .	1.0484	1.0485 (*4*) 1.0486 (*11*)

Table II. Performance Data for Solubility Apparatus

Partial Pressure of Gas: 1 Atm. Solubility in Bunsen Coefficient

Gas	Liquid	T, ° C	Average solubility	Absolute av dev, %	Solubility literature
CO_2	H_2O	0.2	1.699	0.18	1.7023 (*9*) 1.714 (*13*) 1.695 (*6*)
		25	0.758	0.13	0.7565 (*9*) 0.761 (*7*) 0.749 (*5*) 0.760 (*13*) 0.758 (*10*) 0.759 (*3*) 0.763 (*6*)
		0.40	0.530	0.38	0.513 (*9*) 0.530 (*7*) 0.530 (*13*) 0.529 (*6*)
C_3H_6	*i*-PrOH	0	38.30	0.13	38.53 (*6*)
		10	26.26	0.23	26.56 (*6*)
		20	19.25	0.31	19.23 (*6*)
	MeOH	30	12.36		12.21 (*6*)
	n-PrOH	30	15.27	0.52	15.24 (*6*)
	i-PrOH	30	14.48	0.21	14.46 (*6*)
		40	10.95		10.92 (*6*)

Table III. Solubility of Cyclopropane in Carboxylic Acids

Partial Pressure of Gas: 1 Atm

		Average solubility		
Acid	T, ° C	Bunsen coeff.	Mol fraction	P_T, mm Hg
Acetic	20	17.54	0.0437	771.09
	30	13.30	0.0338	779.61
	40	10.77	0.0279	793.20
Propionic	0	50.99	0.1445	760.26
	10	34.69	0.1041	761.43
	20	24.22	0.0759	762.31
	30	18.66	0.0602	765.73
	40	14.40	0.0476	770.10
n-Butyric	0	54.10	0.1816	760.04
	10	36.29	0.1307	760.22
	20	25.87	0.0977	760.68
	30	19.58	0.0765	761.39
	40	14.96	0.0601	762.54
i-Butyric	0	56.76	0.1904	760.08
	10	38.51	0.1388	760.43
	20	27.17	0.1030	761.35
	30	20.43	0.0802	762.62
	40	15.78	0.0637	764.78
n-Valeric	0	52.36	0.2031	760.02
	10	35.17	0.1474	760.04
	20	25.49	0.1123	760.09
	30	19.06	0.0872	760.55
	40	14.75	0.0694	760.88

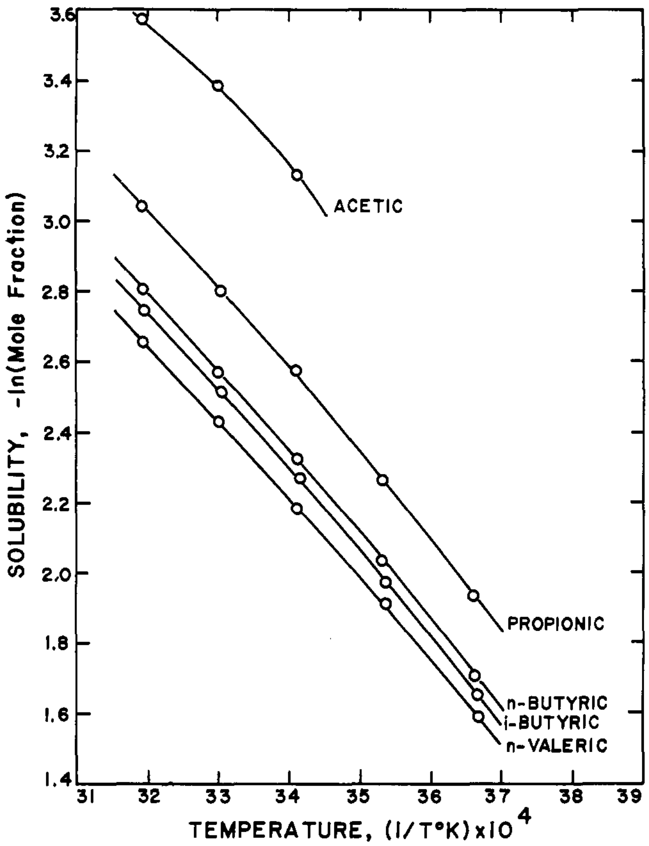

Figure 1. Variation of solubilities of cyclopropane in carboxylic acids with temperature

of the same order of magnitude as for cyclopropane in the carboxylic acids over the same temperature range. These performance data are also presented in Table II and are in good agreement with the values of Loeffler and McKetta. These solubilities, as well, confirm the reproducibility of the apparatus with a maximum deviation of ±0.5% from the mean of several measurements under equivalent experimental conditions.

The solubilities of cyclopropane gas in acetic, propionic, *n*-butyric, *i*-butyric, and *n*-valeric acids over the temperature range of 0–40°C at a gas partial pressure of 1 atm have been determined. These data, expressed in both Bunsen coefficient and mole fraction based on the monomer acid molecular weight are presented in Table III. In most cases, the values reported in Table III are the averages of three experimental determinations. For a total of 65 runs, the maximum deviation of the solubility from the mean for cyclopropane in a given acid at the same temperature is less than the estimated experimental error 0.5%.

The variation of solubility with temperature can be shown by plotting the negative values of the logarithm of the solubility data against the reciprocal of the absolute temperature given in Figure 1. The relationship is almost linear, but increasingly deviates from linearity from *n*-valeric acid to lower acids. The deviation becomes appreciable for acetic acid. The figure also shows that the solubility increases quickly with increasing molecular weight for lower acids and less rapidly for higher acids. Similar results were given by Loeffler (*6*) in his study of the solubility of cyclopropane in alcohols.

Reliable densities for propionic and *n*-valeric acids were not available in the literature. They have been determined in this work, employing a Mettler micrometer balance and a mercury-in-glass calibrated plummet suspended by a platinum wire into the liquid. Densities measured in this work as well as several literature values for the carboxylic acids are presented in Table IV.

Table IV. Densities of Carboxylic Acids

T, °C	Density, g/ml Acetic	Propionic	*n*-Butyric	*i*-Butyric	*n*-Valeric
0		1.0183	0.9776 (*12*)	0.9682 (*12*)	0.9549
10		1.0064	0.9669	0.9584	0.9459
20	1.0491	0.9945	0.9565	0.9482	0.9373
30	1.0381	0.9829	0.9480 (*12*)	0.9379	0.9278
40	1.0284 (*12*)	0.9711	0.9377 (*12*)	0.9305	0.9190

LITERATURE CITED

(1) Barton, J. R., PhD Dissertation, Chemical Engineering Department, Queen's University, Kingston, Ontario, 1970.
(2) Battino, R., Clever, H. L., *Chem. Rev.*, **66**, 395 (1966).
(3) Bohr, Chr., *Wied. Ann.*, **68**, 504 (1899).
(4) Handbook of Chemistry and Physics, 50th ed., pp E232, C78, C215, C445, C451, C411, Chemical Rubber Co., Cleveland, Ohio, 1969–70.
(5) Houghton, G., McLean, A. M., Ritchie, P. D., *Chem. Eng. Sci.*, **6**, 132 (1957).
(6) Loeffler, C. E., McKetta, J. J., *A.I.Ch.E. J.*, **12**, 813 (1966).
(7) Loprest, F. J., *J. Phys. Chem.*, **61**, 1128 (1957).
(8) Markam, A. E., Kobe, K. A., *Chem. Rev.*, **28**, 519 (1941).
(9) Markam, A. E., Kobe, K. A., *J. Amer. Chem. Soc.*, **63**, 449 (1941).
(10) Robb, R. A., Zimmer, M. F., *J. Chem. Eng. Data*, **13**, 200 (1968).
(11) Scheflan, L., Jacobs, M. B., "The Handbook of Solvents," pp 83, 607, 183, 467, Van Nostrand, New York, N.Y., 1953.
(12) Timmermans, J., "Physico-Chemical Constants of Pure Organic Components," Vol 2, pp 278, 279, Elsevier Publishing Co., Amsterdam, Netherlands, 1965.
(13) Yen, L. C., McKetta, J. J., *A.I.Ch.E. J.*, **8**, 501 (1962).
(14) Yen, L. C., McKetta, J. J., *J. Chem. Eng. Data*, **7**, 288 (1962).

RECEIVED for review July 13, 1970. Accepted October 2, 1970. This study was supported by the National Research Council of Canada Grant No. A-2473.