librium ratios are also tabulated in Table I and shown in Figure 4.

Discussion

The four temperatures chosen for studying this binary system all lie between the critical temperatures for the two pure components. Since the equilibrium ratios for the two components converge to unity at the critical pressure of the binary mixture that has the experimental temperature as its critical temperature, it is possible to obtain the critical pressure corresponding to each experimental temperature from the *K–P* plot. These values are presented graphically in Figure 5.

As indicated earlier, one of the primary objectives of this work was to obtain the binary interaction parameter for systems containing carbon dioxide and toluene. The usual method for determining the interaction parameter is to find the value which will give the minimum deviation between the experimental bubble point locus and the bubble point locus predicted by an equation of state. The value determined this way normally gives a good prediction of the dew point locus as well. As an example, the interaction parameter δ_{ij} in the relationship

$$a_m = (1 - \delta_{ij})(a_i a_j)^{1/2}$$

for evaluating the parameter a_m for the Peng–Robinson (*4*) equation of state was found to be 0.09 for the toluene–carbon dioxide binary. Within a range of pressures up to 90% of the critical, the average absolute difference between the experimental and predicted bubble point pressure is 20.3 psi, and the average arithmetic difference is −7.8 psi.

Literature Cited

(1) Fredenslund, A., Mollerup, J., Christiansen, L. J., *Cryogenics*, **13**, 414 (1973).
(2) Kalra, H., Kubota, H., Robinson, D. B., Ng, H.-J., *J. Chem. Eng. Data*, **23**, 317 (1978).
(3) Kalra, H., Robinson, D. B., *Cryogenics*, **15**, 409 (1975).
(4) Peng, D.-Y., Robinson, D. B., *Ind. Eng. Chem. Fundam.*, **15**, 59 (1976).

Received for review February 14, 1978. Accepted July 11, 1978. The financial support received for this work from the Gas Processors Association, Tulsa, Okla., and the Hydrocarbon Research Center at the University of Alberta is gratefully acknowledged.

Ionization Constant of Mandelic Acid and Some of Its Derivatives[†]

Joseph J. Klingenberg,* Doris S. Knecht, Anne E. Harrington, and Ralph L. Meyer

Department of Chemistry, Xavier University, Cincinnati, Ohio 45207

The ionization constants of mandelic acid and 16 of its derivatives were measured in aqueous solution at 25 °C using the potentiometric method described by Albert and Serjeant.

Ionization constants have been determined for only a relatively small number of mandelic acid derivatives. Prior to 1966 values had been reported only for mandelic acid (*7*) and *m*-halo (*7*), *o*-, *m*-, and *p*-nitro (*3*), and *p*-bromo (*2*) derivatives of mandelic acid. In 1966 Klingenberg, Thole, and Lingg (*5*) published ionization constant values for 13 mandelic acid derivatives. Table I is a summary of the values reported. The ionization constants of nine additional derivatives have been determined. Results obtained for mandelic acid and seven of the previously reported derivatives are also given.

Experimental Section

The acids used in this work (Table II) were synthesized by methods appearing in the literature except for mandelic acid and *m*-hydroxy- and 4-hydroxy-3-methoxymandelic acids which were purchased from commercial sources.

Ionization constants were measured potentiometrically by the procedure given in Albert and Serjeant (*1*). This consists essentially in the measurement of the pH of a solution of a known concentration of the test acid after addition of successive increments of standard base until the equivalence point is reached. The ionization constant is calculated from the equation

$$pK_a^M = pH + \log \frac{[HA] - \{H^+\}}{[A^-] + \{H^+\}}$$

Table I. Previously Reported Ionization Constants of Mandelic Acid and Its Derivatives at 25 °C

acid[a]	method[b]	pK_a	type[c]	ref
p-nitromandelic	con.	2.98	T	3
m-nitromandelic	con.	3.03	T	3
p-iodomandelic	pot.	3.14	M	5
o-nitromandelic	con.	3.15	T	3
p-chloromandelic	pot.	3.15	M	5
p-bromomandelic[d]	pot.	3.15	M	5
p-fluoromandelic	pot.	3.19	M	5
m-bromomandelic	con.	3.23	T	7
m-chloromandelic	con.	3.24	T	7
m-fluoromandelic	con.	3.24	T	7
m-iodomandelic	con.	3.26	T	7
o-fluoromandelic	pot.	3.30	M	5
o-chloromandelic	pot.	3.31	M	5
o-bromomandelic	pot.	3.32	M	5
mandelic[e]	con.	3.41	T	7
p-methoxymandelic	pot.	3.42	M	5
p-ethylmandelic	pot.	3.55	M	5
2,5-dimethylmandelic	pot.	3.57	M	5
p-*n*-butylmandelic	pot.	3.58	M	5
p-isopropylmandelic	pot.	3.64	M	5
o-methoxymandelic	pot.	3.64	M	5

[a] Concentration 0.01 M. [b] Key: con. = conductometric, pot. = potentiometric. [c] Key: T = thermodynamic, M = mixed. [d] A pK_a of 3.39 reported at 18 °C (*7*). [e] A pK_a of 3.06 reported at 18 °C (*2*).

where [HA] is the stoichiometric concentration of the undissociated acid molecular, $[A^-]$ is the stoichiometric concentration of the anion, and $\{H^+\}$ is the activity of the hydrogen ion as calculated from the measured pH. The constant so obtained is a "mixed" constant since both concentration and activity terms are used. The thermodynamic constant can be obtained from the equation

$$pK_a^T = pK_a^M \pm \frac{0.507\sqrt{I}}{1 + 1.6\sqrt{I}}$$

[†] Based on dissertations submitted by D. S. Knecht, A. E. Harrington, and R. L. Meyer to the Department of Chemistry of Xavier University in partial fulfillment of the requirements for the degree of Master of Science.

0021-9568/78/1723-0327$01.00/0

Table II. Preparation, Melting Points, and Ionization Constants of Mandelic Acid and Derivatives at 25 °C

acid (0.010 M)	melting point, °C lit.	melting point, °C exptl[a]	pK_a^T	source of data[b]
2,4-dichloromandelic	120–121	120–121	3.12 ± 0.05[c]	8
		119–121	3.29 ± 0.14	4
3,4-dichloromandelic	113–115	114–114.5	3.13 ± 0.05	6
p-chloromandelic	120–121	120–121	3.22 ± 0.06	6
m-nitromandelic	119–120	114–118	3.28 ± 0.04	4
p-bromomandelic	117–119	116–118	3.28 ± 0.02	8
p-nitromandelic	126–127	124–127	3.34 ± 0.04	4
m-hydroxymandelic	131–132	130–132	3.38 ± 0.02	8
		130–130.5	3.39 ± 0.04	6
m-chloromandelic	115–115.5	114–115.5	3.39 ± 0.02	4
mandelic	118–120	118–120	3.39 ± 0.01	8
		118–120	3.40 ± 0.01	8
		120–121	3.40 ± 0.04	6
4-hydroxy-3-methoxymandelic	132–134	133–135	3.42 ± 0.03	8
o-nitromandelic	138–140	137–141	3.44 ± 0.02	4
m-bromomandelic	113–116	109–110	3.44 ± 0.03	4
m-methylmandelic	111–112	111–112	3.45 ± 0.03	6
p-methylmandelic	145–145.5	145–146	3.46 ± 0.04	6
p-trifluoromethylmandelic	129–130	129–130.5	3.53 ± 0.09	4
2,4,6-trimethylmandelic	132–134	133–135	3.61 ± 0.05	6
p-phenylmandelic	201–203	194–198	3.79 ± 0.04	8

[a] As determined with the Fisher-Johns melting point apparatus. Thermometer calibrated against standards of known melting point. [b] Preparation or procurement of these acids described in the theses indicated. References to original literature sources are also given. [c] Obtained by taking antilogarithms of each pK_a value in the set of results, averaging these, and writing down the logarithm of the average as pK_a. The largest deviation between this value and any value in the set is written after the pK_a as its scatter (*1*).

where I, the ionic strength, is equal to $0.5 \sum cz^2$ with c equal to the molar concentration of the ions involved and z equal to their valency. The thermodynamic constant can be estimated from the equation $pK_a^T = pK_a^M \pm 0.5(I_m^{1/2})$ where I_m is the ionic strength at the mid-point in the titration. Since $I_m \simeq 0.005$ for a 0.01 M titration as used in this work the values of pK_a^M and pK_a^T differ by about 0.035 pK units. The results are tabulated in Table II.

Literature Cited

(1) Albert, A. A., Serjeant, E. P., "Ionization Constants of Acids and Bases", Wiley, New York, N.Y., 1962.
(2) Alimarin, I. P., Shen, H.-H., *Vestn. Mosk. Univ., Khim.*, **15**, (6), 39–41 (1960).
(3) Grimsell, E., *Ark. Kemi, Mineral. Geol.*, **15** (17), 1–10 (1942).
(4) Harrington, A. E., M.S. Thesis, Xavier University, Cincinnati, Ohio, 1974.
(5) Klingenberg, J. J., Thole, J. P., Lingg, J. D., *J. Chem. Eng. Data*, **11**, 94 (1966).
(6) Knecht, D. S., M.S. Thesis, Xavier University, Cincinnati, Ohio, 1968.
(7) Kortum, G., Vogel, W., Andrussow, K., "Dissociation Constants of Organic Acids in Aqueous Solution", Butterworths, London, 1961.
(8) Meyer, R. L., M.S. Thesis, Xavier University, Cincinnati, Ohio, 1977.

Received for review March 31, 1978. Accepted July 1, 1978.

Effect of Pressure on the Viscosity of Aqueous NaCl Solutions in the Temperature Range 20–150 °C

Joseph Kestin,* H. Ezzat Khalifa, Yoshiyuki Abe, Clifford E. Grimes, Heros Sookiazian, and William A. Wakeham

Division of Engineering, Brown University, Providence, Rhode Island 02912

The paper presents a detailed study of the effect of pressure on the viscosity of aqueous NaCl solutions in the range 20–150 °C and the concentration range 0–5.4 *m*. The viscosity was measured by the oscillating-disk method in the pressure range 0–30 MPa at six concentrations along a large number of isotherms. The experimental results have an estimated uncertainty of ±0.5%. The results constitute the first measurements of the viscosity of NaCl solutions over an extended range of pressure, temperature, and concentration. The experimental data have been correlated in terms of pressure, temperature, and concentration. The correlation reproduces the original data to within the quoted uncertainty. The paper includes comparisons between the correlation and the experimental results of other investigators.

1. Introduction

It is now recognized that a knowledge of the viscosity of concentrated aqueous salt solutions is required for a number of geophysical and engineering applications. For example, the measurement of the permeability of porous media requires this knowledge for its evaluation. Similar data are needed for the calculation of the motion of geothermal fluids through wells and ducts, for the modeling of geothermal reservoirs, and for the design of extraction and power generation equipment for the utilization of geothermal energy.

On the other hand, a review of available literature (*2*, *17*) shows that measurements of the pressure effect are nonexistent for any solutions, except for our earlier work on NaCl (*7*). At atmospheric pressure there exist abundant data for NaCl and KCl solutions (*2*, *17*) which, however, do not reach beyond a

0021-9568/78/1723-0328$01.00/0