T degrees Celsius, °C

Literature Cited

(1) Lyon, R. N., Kolstad, G. A., Eds., "A Recommended Research Program in Geothermal Chemistry", WASH-1344, Department of Energy, Washington, DC, 1974.
(2) Silvester, L. F., Pitzer, K. S., *J. Phys. Chem.*, **81**, 1822 (1977).
(3) Fabuss, B. M., Korosi, A., "Properties of Sea Water and Solutions Containing Sodium Chloride, Potassium Chloride, Sodium Sulphate and Magnesium Sulfate", Office of Saline Water Research and Development Progress Report, **No. 384**, Washington, DC, 1968.
(4) Korosi, A., Fabuss, B. M., "Thermophysical Properties of Saline Water", Office of Saline Water Research and Development Progress Report, No. 363, Washington, DC, 1968.
(5) Yusufova, V. D., Pepinov, R. I., Nikolaev, V. A., Guseinov, G. M., *Inzh.-Fiz. Zh.*, **29**, 600 (1975).
(6) Rowe, A. M., Chou, J. C. S., *J. Chem. Eng. Data*, **15**, 61 (1970).
(7) Haywood, R. W., *J. Eng. Power*, **88**, 63 (1966).
(8) Kestin, J., Whitelaw, J. H., *J. Eng. Power*, **88**, 82 (1966).
(9) Touloukian, Y. S., Liley, P. E., Saxena, S. C., "Thermal Conductivity", Vol. 3, IFI/Plenum Data Corp., New York, 1970.
(10) Riedel, L., *Chem.-Ing.-Tech.*, **23**, 59 (1951).
(11) Jamieson, D. T., Irving, J. B., Tudhope, J. S., "Liquid Thermal Conductivity: a Data Survey to 1973", HMSO, Edinburgh, 1975.
(12) Jamieson, D. T., Tudhope, J. S., *Desalination*, **8**, 393 (1970).
(13) Washburn, E. W., Ed., "International Critical Tables", Vol. V, McGraw-Hill, New York, 1929.
(14) Vargaftik, N. B., Os'minin, Yu. P., *Teploenergetika* (*Moscow*), **3**, 11 (1956).
(15) Chernyshev, A. K., *Tr. GIAP*, **No. 41**, 65 (1976); *Chem. Abstr.*, **91**, 500 (1979).
(16) Unterberg, W., "Thermophysical Properties of Aqueous Sodium Chloride Solutions", Report No. 64-21, May 1964, Department of Engineering, University of California, Los Angeles, Los Angeles, CA.
(17) Chernen'kaya, E. I., Vernigora, G. A., *Zh. Prikl. Khim.* (*Leningrad*), **45**, 1704 (1972).
(18) Tufeu, R., LeNeindre, B., Johannin, P., *C. R. Hebd. Seances Acad. Sci., Ser. B*, **262**, 229 (1966).
(19) Chiquillo, A., "A Measurement of the Relative Thermal Conductivities of Aqueous Salt Solutions by a Non-Steady State Hot-Wire Method", Thesis No. 3955, Eidg. Technische Hochschule, Zurich, Switzerland, 1967.
(20) Kaputinski, A. F., Ruzavin, I. I., *Zh. Fiz. Khim.*, **29**, 2222 (1955).
(21) Predvoditelev, A. S., *Zh. Fiz. Khim.*, **22**, 339 (1948).
(22) Fatullaev, F. G., Kerimov, A. M., *Russ. J. Phys. Chem.* (*Engl. Transl.*), **47**, 913 (1973).
(23) Jamieson, D. T., *J. Chem. Eng. Data*, **24**, 244 (1979).
(24) Verba, O. I., Gruzdev, V. A., Genrikh, V. N., Zakharenko, L. G., Lavrov, V. A., Psakhis, B. I., *Issled. Teplofiz. Svoistv. Zhidk. Rastvorov Splavov*, 40-59 (1977).

Received for review October 15, 1979. Accepted February 19, 1980. Supported by the U. S. Department of Energy, Office of Basic Energy Science, Division of Engineering, Mathematical and Geosciences under Contract W-7405-ENG-48.

Review of Density Estimation of Saturated Liquid Mixtures

Doddipatla Veeranna and Devinder N. Rihani*

Engineers India Ltd., New Delhi 110 001, India

Various correlations with regard to the density model and mixing rules needed for this purpose have been reviewed. It has been found that the modified Rackett equation with the Chueh–Prausnitz mixing rule, which predicts the density within 3%, should be acceptable from an engineering design standpoint. A total of 3600 data points from 88 systems (containing polar and nonpolar constituents) were tested. The data extended well into the critical region for systems with nonpolar components. Whenever polar compounds were present, this was generally in the T_r range of 0.4–0.7 and to that extent the validity of this exercise would be limiting.

1. Introduction

Density is a parameter affecting directly or indirectly every stage of the process design activity. For pure components a large volume of liquid density data has been reported in standard handbooks (*1–4*), etc. However, such is not the case with mixtures where, besides temperature and pressure, composition is also one of the variables. For mixtures the required data are seldom available; it is necessary to reduce and correlate the data for meaningful interpolations. The utility of having a reliable estimation tool can be easily realized if we consider that for an actual system the number of components to be handled may be more than 10—say for the case of a C_8 aromatics separation train this could be close to 20, with some of them being supercritical.

This paper presents the results of a study undertaken to review the estimation procedures for mixtures containing nonpolar and polar components. Attention was given to criteria like (i) accuracy, (ii) range of application, (iii) ease of use, and (iv) availability of input parameters. For use with a computerized thermophysical property package, it would be advantageous to have a method based on common input parameters, i.e., critical properties, acentric factor, etc., which are normally available or can be estimated with a high degree of reliability.

2. Available Correlations

The estimation method may utilize either an equation of state like Redlich–Kwong, BWR, etc., or the corresponding states approach. The latter is preferred because of wider applicability and lesser computational efforts. This paper is also restricted to the corresponding states approach.

2.1 Nonpolar Systems. On the basis of the work of many authors (*5–12*) it was decided to limit this investigation to testing with the following correlations.

(a) Harmens Equation (9). Originally Harmens tabulated $F(T_r)$ as a function of reduced temperature in the range $0.3 \leq T_r \leq 0.96$. Spencer and Danner (*5*) enhanced its usage by converting it into an analytical form.

(b) Modified Rackett Equation (5). The original equation by Rackett (*13*) has been modified (*14*, *23*) and extended to mixtures. It employs critical temperature, pressure, and an adjustable parameter called the Rackett parameter, Z_{RA}, as shown.

$$V = \frac{RT_c}{P_c} Z_{RA}^{1+(1-T_r)^{2/7}} \tag{1}$$

$$V_m = R\left[\sum_{i=1}^{n} \frac{x_i T_{ci}}{P_{ci}}\right] Z_{RAm}^{1+(1-T_r)^{2/7}} \tag{2}$$

$$Z_{RAm} = \sum_{i=1}^{n} x_i Z_{RAi} \tag{3}$$

$$T_r = T/T_{cm} \tag{4}$$

T_{cm}, pseudocritical temperature for mixtures, was obtained through one of the mixing rules mentioned later on.

(c) Generalized Guggenheim Equation (6). The original Guggenheim equation has been generalized by correlating the two constants a and b as functions of acentric factor by Chiu et al. It uses the concept of scaling volume as the correlating parameter in preference to the critical volume.

Essentially, all these equations were originally developed for pure components and later on extended to mixtures. The mixing rules used for evaluating various parameters are likely to play a significant role. The important parameter in the present case is pseudocritical temperature. A reference to the literature indicated the suitability of the following mixture rules.

(1) Harmens (9). It uses a mean of mole fraction and weight fraction for averaging purposes.

(2) Chiu et al. (6). Weighting factors based on critical temperatures and acentric factors were recommended for use with the Guggenheim equation.

(3) Chueh-Prausnitz (15). This was originally proposed for use with the modified Redlich-Kwong equation for prediction of phase behavior. Spencer and Danner (5) adopted this, for use with the modified Rackett equation. The interaction parameter, k_{ij}, has been reported for some pairs while for others this may be estimated. The equations for this are as follows:

$$T_{cm} = \sum_{i=1}^{n}\sum_{j=1}^{n} \phi_i \phi_j T_{cij} \tag{5}$$

$$\phi_i = \frac{x_i V_{ci}}{\sum_{j=1}^{n} x_j V_{cj}} \tag{6}$$

$$T_{cij} = (T_{ci} T_{cj})^{1/2}(1 - k_{ij}) \tag{7}$$

(4) Barner and Quinlan (16). In an attempt toward more reliable pseudocritical constants for enthalpy and density predictions, a new binary interaction parameter k'_{ij} was introduced. For the systems where k'_{ij} is unity, the correlation reduces to the well-known Kay's mixing rule.

(5) Lee and Kesler (17). This method utilizes individual component properties without binary parameters, for estimation of pseudocritical properties.

(6) Li (18). This involves averaging critical temperature on critical volume fraction basis. It was originally proposed for estimating the true critical temperature.

2.2 Polar Systems. Not much information has been published about mixtures containing these compounds. Reid et al. (19) recommend the use of the Yen and Woods correlation (8). Halm and Stiel (20) advocate the use of a fourth parameter for correlation of pure component data. The Joffe and Zudkevitch (21) method uses two fitted constants.

For evaluation purposes the method of Yen and Woods was not considered since it was basically developed for nonpolar substances and Spencer and Danner (14) have reported large errors with this correlation even for pure hydrocarbons. The Joffe and Zudkevitch method was also dropped because it (i) requires two arbitrary constants for each of the components involved in the mixture and (ii) uses critical volumes, which can be in large errors for polar substances. Correlation of Halm and Stiel has been tested in the present work by extending it to mixtures. Constants $V^{(0)}$ to $V^{(5)}$ were fitted as a function of T_r for use with machine computations. On the basis of earlier experience with nonpoar systems it was decided to use only the Chueh-Prausnitz mixing rule for estimation of pseudocritical temperature and the modified Prausnitz and Gunn mixing rule (19) for pseudocritical pressure.

From the application point of view it would be desirable to have a single correlation which is valid for mixtures of all components irrespective of the polarity. It was thus considered worthwhile to explore the possibility of using the three earlier models as well (section 2.1).

3. Data Sources. Table I gives the details of the various systems for which the experimental data have been tested. Pure component data needed for this purpose were obtained as follows: (i) Critical temperature, pressure, volume, compressibility, and acentric factor were taken from ref 3 and 19. (ii) Constant C for use in the Harmens equation was estimated through the recommended correlation, whenever it was not available in the original reference. Modifications advocated by Harmens for the presence of methane and nitrogen were not found to be necessary. (iii) Z_{RA} was taken from ref 14, wherever available; otherwise this was estimated from the experimental density data by using either a nonlinear optimization program or a single point estimation through eq 1. The estimated values are given in Table II. Recently, Spencer and Adler (23) reported data for a large number of compounds. However, this could not be adopted for the present purpose since it was published after the completion of this work. In general the Z_{RA} values are quite comparable. (iv) V_{SC} was obtained from the work of Gunn and Yamada (22). When not available, it was estimated through pure component density data. (v) To account for the presence of quantum gases the various parameters were adjusted as recommended by Chueh and Prausnitz (15). (vi) The X parameter for using the Halm and Stiel equation has been tabulated in ref 20; for others it was estimated.

4. Results

4.1 Nonpolar Systems. A preliminary analysis of the data indicated consistently larger errors with the Barner-Quinlan and Lee-Kesler mixing rules, when used in conjunction with various density models. Table III shows deviations for some of the systems chosen at random. These mixing rules were thus dropped from further analysis.

Out of a total of 2796 data points tested, the number of points that could be handled by various mixing rules is shown in Table IV. The Li mixing rule which was originally proposed for estimation of true critical temperature was applicable for a maximum number of points (2741) while the mixing rule of Barner and Quinlan accepted the lowest numer of points (2497). In an actual case this could sometimes become a limitation when one is working in the critical range. Use of one or the other mixing rule for pseudocritical temperature may decide the phase of the system and also the validity of the density model.

For hydrogen- and helium-bearing systems the quantum correction approach showed lower deviations and is recommended for use. However this observation is based on limited published data and should be used with caution.

Percentage average and maximum deviation for various density models were determined. In an attempt to analyze these as a function of T_r, as shown in Table IV, the following observations could be made.

(i) Region I: $T_r \leq 0.4$. The number of points in this region were negligible to draw any meaningful conclusion. These are not included in the table.

(ii) Region II: $0.4 < T_r \leq 0.95$. The maximum number of points (approximately 80%) were found to lie in this region. The lowest deviation (2.28%) was observed for the modified Rackett equation using the mixing rule of Chueh-Prausnitz. The Harmens equation with the same mixing rule was the second lowest (2.34%). Even though this temperature range is far removed from the critical, maximum deviations are noticed to be quite large. No particular trend in maximum deviation could be noticed, except that it occurred generally at higher T_r values. Most of the systems, including inorganics like CO_2 and H_2S, showed maximum deviations to be less than 10%. The CO_2-eicosane system showed consistently high deviations for all the cases. It could be an indication of the data error.

(iii) Region III: $0.95 < T_r < 1.00$. The generalized Guggenheim equation in conjunction with the Chueh-Prausnitz mixing

Table I. Data Sources

system no.	system	ref	system no.	system	ref
				(a) Nonpolar Systems	
1	methane–ethane	*a*	31	propane–benzene	*y*
2	–propane	*b*	32	–*n*-octane	*z*
3	–*n*-butane	*i*	33	–*n*-decane	*aa*
4	–isobutane	*c*	34	*n*-butane–isobutane	*l*
5	–*n*-pentane	*d*	35	–*n*-octane	*z*
6	–*n*-octane	*e*	36	–*n*-decane	*bb*
7	–*n*-nonane	*f*	37	carbon dioxide–ethane	*cc*
8	–*n*-decane	*g*	38	–propane	*t*
9	–ethane–propane	*a*	39	–*n*-butane	*t*
10	–propane–*n*-decane	*h*	40	–isobutane	*dd*
11	–ethane–propane–*n*-butane–*n*-pentane	*bbb*	41	–*n*-pentane	*ee*
12	–ethane–propane–*n*-pentane–*n*-hexane	*bbb*	42	–*n*-decane	*ff*
13	ethene–*n*-heptane	*j*	43	–*n*-eicosane	*gg*
14	ethane–propene	*k*	44	–hydrogen sulfide	*hh*
15	–propane	*l*	45	hydrogen sulfide–methane	*t*
16	–*n*-butane	*m*	46	–ethane	*ii*
17	–isobutane	*n*	47	–propane	*jj*
18	–*n*-pentane	*o*	48	–isobutane	*kk*
19	–cyclohexane	*p*	49	–*n*-pentane	*ll*
20	–*n*-heptane	*q*	50	–*n*-decane	*t*
21	–*n*-octane	*r*	51	–nitrogen	*mm*
22	–*n*-decane	*s*	52	nitrogen–methane	*a*
23	propene–propane	*t*	53	–methane–ethane	*a*
24	propene–1-butene	*u*	54	–methane–propane	*a*
25	propane–*n*-butane	*v*	55	–methane–ethane–propane	*nn*
26	–*n*-butane	*l*	56	–methane–ethane–propane–*n*-butane–*n*-pentane–*n*-hexane	*nn*
27	–isobutane	*l*	57	–helium–methane–ethane–propane	*nn*
28	–*n*-pentane	*v*	58	–helium–methane–ethane–propane–*n*-butane	*nn*
29	–isopentane	*w*	59	–helium–methane–ethane–propane–*n*-butane–*n*-pentane–*n*-hexane–*n*-heptane	*nn*
30	–*n*-hexane	*x*			
			60	hydrogen–*n*-hexane	*oo*
				(b) Systems with Polar Compounds	
61	acetic acid–acetone	*pp*	75	2-butanol–carbon tetrachloride	*ww*
62	–methyl isobutyl ketone	*qq*	76	carbon tetrachloride–1-heptanol	*ww*
63	–toluene	*aaa*	77	–methanol	*ww*
64	acetone–benzene	*pp*	78	–1-octanol	*ww*
65	–ethanol	*aaa*	79	–3-methylbutanol	*ww*
66	–methanol	*aaa*	80	–1-pentanol	*ww*
67	–1-propanol	*aaa*	81	–2-methyl-2-butanol	*ww*
68	–toluene	*qq*	82	–2-propanol	*ww*
69	–water	*yy*	83	–1-propanol	*ww*
70	–water	*zz*	84	chloroform–ethene	*rr*
71	benzene–chloroform	*tt*	85	ethane–methanol	*vv*
72	2-methylpropanol–carbon tetrachloride	*ww*	86	methanol–water	*zz*
73	1-butanol–carbon tetrachloride	*ww*	87	monoethanolamine–water	*xx*
74	1-butanol–methyl isobutyl ketone	*ss*	88	1-propanol–water	*uu*

[a] Rodosevich, J. B., Miller, R. C., *AIChE J.,* **19,** 729 (1973). [b] Huang, E. T. S., Swift, G. W., Kurata, F., *ibid.,* **13,** 846 (1967). [c] Olds, R. H., Sage, B. H., Lacey, W. N., *Ind. Eng. Chem.,* **34,** 1008 (1942). [d] Sage, B. H., Reamer, H. H., Olds, R. H., Lacey, W. N., *ibid.,* **34,** 1108 (1942). [e] Kohn, J. P., Bradish, W. F., *J. Chem. Eng. Data,* **9,** 5 (1964). [f] Shipman, L. M., Kohn, J. P., *ibid.,* **11,** 176 (1966). [g] Sage, B. H., Lavender, H. M., Lacey, W. N., *Ind. Eng. Chem.,* **32,** 743 (1940). [h] Wiese, H. C., Reamer, H. H., Sage, B. H., *J. Chem. Eng. Data,* **15,** 75 (1970). [i] Sage, B. H., Budenholzer, R. A., Lacey W. N., *Ind. Eng. Chem.,* **32,** 1262 (1940). [j] Kay, W. B., *ibid.,* **40,** 1459 (1948). [k] McKay, R. A., Reamer, H. H., Sage, B. H., Lacey, W. N., *ibid.,* **43,** 2112 (1951). [l] Kahre, L. C., *J. Chem. Eng. Data,* **18,** 267 (1973). [m] Kay, W. B., *Ind. Eng. Chem.,* **32,** 353 (1940). [n] Besserer, G. J., Robinson, D. B., *J. Chem. Eng. Data,* **18,** 301 (1973). [o] Reamer, H. H., Sage, B. H., Lacey, W. N., *ibid.,* **5,** 44 (1960). [p] Kay, W. B., Albert, R. E., *Ind. Eng. Chem.,* **48,** 422 (1956). [q] Kay, W. B., *ibid.,* **30,** 459 (1938). [r] Rodrigues, A. B. J., McCaffrey, D. S., Jr., Kohn, J. P., *J. Chem. Eng. Data,* **13,** 164 (1968). [s] Reamer, H. H., Sage, B. H., *ibid.,* 7, 161 (1962). [t] Sage, B. H., Lacey, W. N., Monograph for API Research Project No. 37, "Some Properties of Lighter Hydrocarbons, Hydrogen Sulfide and Carbon Dioxide", American Petroleum Institute, Washington, D.C., 1955. [u] Goff, G. H., Farrington, P. S., Sage, B. H., *Ind. Eng. Chem.,* **42,** 735 (1950). [v] Kay, W. B., *J. Chem. Eng. Data,* **15,** 46 (1970). [w] Vaughan, W. E., Collins, F. C., *Ind. Eng. Chem.,* **34,** 885 (1942). [x] Kay, W. B., *J. Chem. Eng. Data,* **16,** 137 (1971). [y] Glanville, J. W., Sage, B. H., Lacey, W. N., *Ind. Eng. Chem.,* **42,** 508 (1950). [z] Kay, W. B., Genco, J., Fichtner, D. A., *J. Chem. Eng. Data,* **19,** 275 (1974). [aa] Reamer, H. H., Sage, B. H., *ibid.,* **11,** 17 (1966). [bb] Reamer, H. H., Sage, B. H., *ibid.,* **9,** 24 (1964). [cc] Gugnoni, R. J., Eldridge, J. W., Okay, V. C., Lee, T. J., *AIChE J.,* **20,** 357 (1974). [dd] Besserer G. J., Robinson, D. B., *J. Chem. Eng. Data,* **18,** 298 (1973). [ee] Besserer, G. J., Robinson, D. B., *ibid.,* **18,** 416 (1973). [ff] Reamer, H. H., Sage, B. H., *ibid.,* **8,** 508 (1963). [gg] Huie, N. C., Luks, K. D., Kohn, J. P., *ibid.,* **18,** 311 (1973). [hh] Kay, W. B., Bierlein, J. A., *Ind. Eng. Chem.,* **45,** 618 (1953). [ii] Kay, W. B., Brice, D. B., *ibid.,* **45,** 615 (1953). [jj] Kay, W. B., Rambosek, G. M., *ibid.,* **45,** 221 (1953). [kk] Besserer, G. J., Robinson, D. B., *J. Chem. Eng. Jpn.,* **8,** 11 (1975). [ll] Reamer, H. H., Sage, B. H., Lacey, W. N., *Ind. Eng. Chem.,* **45,** 1805 (1953). [mm] Besserer, G. J., Robinson, D. B., *J. Chem. Eng. Data,* **20,** 157 (1975). [nn] Gonzalez, M. H., Lee, A. L., *ibid.,* **13,** 172 (1968). [oo] Nichols, W. B., Reamer, H. H., Sage, B. H., *AIChE J.,* **3,** 262 (1957). [pp] Howard, K. S., Pike, F. P., *J. Chem. Eng. Data,* **4,** 331 (1959). [qq] Hafez, M., Hartlands, S., *ibid.,* **21,** 179 (1976). [rr] Shim, J., Kohn, J. P., *ibid.,* **9,** 1 (1964). [ss] Murty, P. D., Rao, K. V., Rao, P. V., Chiranjivi, C., *ibid.,* **18,** 39 (1973). [tt] Sanni, S. A., Hutchison, P., *ibid.,* **18,** 317 (1973). [uu] Mikhail, S. J., Kimal, W. R., *ibid.,* **8,** 323 (1963). [vv] Ma, Y. H., Kohn, J. P., *ibid.,* **9,** 3 (1964). [ww] Gold, P. I., Perrine, R. L., *ibid.,* **12,** 5 (1967). [xx] Tseng, Y. M., Thompson, A. R., *J. Chem. Eng. Data,* **9,** 264 (1964). [yy] Thomas, K. T., McAllister, R. A., *AIChE J.,* **3.** 161 (1957). [zz] Yegrovich, T. W., Swift, G. W., Kurata, F., *J. Chem. Eng. Data,* **16,** 222 (1971). [aaa] Hellwege, K. H., "Landolt-Bornstein, Numerical Data and Functional Relationships in Science and Technology, Group IV", Vol. 1, Densities of Liquid Systems Part a, Springer Verlag, Berlin, 1974. [bbb] Hanson, G. H., Kuist, B. B., Brown, G. G., *Ind. Eng. Chem.,* **36,** 1161 (1944).

rule gave the lowest error (6.14%), followed closely by the modified Rackett equation (6.18%) using the same mixing rule. The Harmens model which was found to be good for region II showed large deviations. This could be due to the extrapolation of the model which was originally developed for the $0.3 \leq T_r \leq 0.96$ range.

For the development of a computerized estimation package it would be desirable to have a single correlation over the entire temperature range, if possible, without sacrificing much of the accuracy. With this objective the data were analyzed, over the entire temperature range. For the 2600 points common to the various mixing rules, the information in Table V was obtained: predictions from the two density correlations, modified Rackett and generalized Guggenheim, using the Chueh–Prausnitz and Li mixing rule, respectively, are quite acceptable for engineering design purposes.

4.2 Polar Systems. On the basis of the analysis for nonpolar systems under 4.1 above, the Barner–Quinlan and Lee–Kessler mixing rules were omitted from this data testing. The Li mixing rule, which has been developed for the critical region, was also not tested as a majority of the experimental data were found to be within the T_r range of 0.4–0.7. Table VI summarizes the results of this analysis. An attempt at extending the Halm and Stiel correlation to mixtures was not successful, due to large errors. The modified Rackett equation in conjunction with the Chueh–Prausnitz mixing rule gave an error of 1.55% for common 824 points which is quite acceptable for engineering design purposes.

5. Summary

For the purpose of this investigation about 3600 experimental data points from 88 systems were analyzed for prediction purposes. It has been found that the modified Rackett equation with the Chueh–Prausnitz mixing rule is suitable for estimation of density of saturated liquid mixtures. The accuracy of the predicted data should be acceptable from an engineering design standpoint.

After submission of this paper a new correlation following the form of Gunn and Yamada equation has been published by Hankinson and Thomson (*24*).

Glossary

k_{ij}	Chueh and Prausnitz binary interaction parameter
P	pressure, atm
R	gas constant, 82.057 atm cm^3/(g-mol K)
T	temperature, K

Table II. Z_{RA} Values for Compounds Estimated in the Present Work

compd	Z_{RA}	compd	Z_{RA}
eicosane	0.2266	3-methylbutanol	0.2619
hydrogen	0.2835[a]	2-methyl-2-butanol	0.2692
helium	0.2854[a]	1-heptanol	0.2554
ethanol	0.2504	1-octanol	0.2858
2-propanol	0.2514	water	0.2377
1-butanol	0.2585	methyl isobutyl ketone	0.2573
2-methylpropanol	0.2619	monoethanolamine	0.2000
2-butanol	0.2553	chloroform	0.2748
1-pentanol	0.2582	carbon tetrachloride	0.2721

[a] Optimized values with quantum correction.

Table III. Results of Preliminary Testing for Various Mixing Rules for T_{cm}

syst no.	points[a]	mixing rule	points[b]	% av dev Harmens	MR[c]	GG[d]
7	131	i Harmens	130	3.99		
		ii Chiu et al.	131			2.90
		iii Chueh–Prausnitz	130	1.47	6.44	5.88
		iv Barner–Quinlan	124	4.65	9.92	9.28
		v Lee-Kesler	123	7.75	13.81	5.00
		vi Li	131	1.73	3.42	3.04
10	87	i	77	3.06		
		ii	87			3.42
		iii	83	2.06	6.83	6.07
		iv	77	4.40	11.96	11.17
		v	74	7.79	16.69	6.45
		vi	87	5.11	3.29	2.78
12	4	i	4	1.81		
		ii	4			3.69
		iii	4	2.79	2.34	2.73
		iv	4	9.30	14.44	14.93
		v	4	9.20	14.19	10.61
		vi	4	7.96	4.97	4.11
22	69	i	61	1.75		
		ii	65			2.39
		iii	61	2.72	2.65	3.26
		iv	59	2.15	6.69	7.26
		v	57	2.54	8.02	2.40
		vi	65	6.06	2.34	3.04
42	78	i	73	3.03		
		ii	78			2.77
		iii	78	4.69	1.76	2.62
		iv	74	2.08	5.89	6.04
		v	75	2.24	7.27	4.86
		vi	78	6.96	2.84	3.95

[a] Number of total points. [b] Number of points accepted. [c] MR = modified Rackett. [d] GG = generalized Guggenheim.

Table IV. Summary of Deviations

	generalized Guggenheim			Harmens			modified Rackett		
	II[a]	III[b]	overall	II[a]	III[b]	overall	II[a]	III[b]	overall
				(a) Chueh–Prausnitz[c]					
(i) no. of points	2155	475	2636	2155	475	2636	2155	475	2636
(ii) % av dev	2.94	6.14	3.29	2.34	6.91	3.12	2.28	6.18	2.72
(iii) % max dev	−21.30	−50.16	−50.16	17.34	31.26	31.26	−22.55	−53.14	−53.14
				(b) Li[c]					
(i) no. of points	2333	400	2741	2333	400	2741	2333	400	2741
(ii) % av dev	3.23	8.53	3.78	3.85	12.28	4.98	3.37	9.10	3.99
(iii) % max dev	36.85	35.82	36.85	37.82	38.66	38.66	37.81	36.31	37.81
				(c) Harmens[c]					
(i) no. of points				2182	429	2614			
(ii) % av dev				2.51	8.89	3.45			
(iii) % max dev				28.38	38.90	38.90			
				(d) Chiu et al.[c]					
(i) no. of points	2232	407	2647						
(ii) % av dev	3.29	6.47	3.75						
(iii) % max dev	48.99	−38.93	48.99						

[a] Region II $0.4 < T_r \leqslant 0.95$. [b] Region III $0.95 < T_r < 1.00$. [c] Mixing rule for pseudocritical temperature.

Table V. Deviations for 2600 Common Points

combination of density correlation and mixing rule for T_{cm}	% av dev
i modified Rackett equation with Chueh-Prausnitz mixing rule	2.67
ii generalized Guggenheim equation with	
(a) Chiu et al. mixing rule	3.55
(b) Li mixing rule	3.32

Table VI. Summary of the Deviations for Polar Systems

	density model			
	generalized Guggenheim	Harmens	modified Rackett	Halm and Stiel
	(a) Chueh-Prausnitz (824)[a]			
(i) % av dev	3.50	2.67	1.55	6.27
(ii) % max dev	−23.30	−26.63	−20.75	−70.50
	(b) Harmens (830)[a]			
(i) % av dev		2.61		
(ii) % max dev		−17.88		
	(c) Chiu et al. (826)[a]			
(i) % av dev	3.19			
(ii) % max dev	−28.39			

[a] Mixing rule for pseudocritical temperature. The numbers in parentheses indicate the number of points.

V	saturated liquid volume, cm^3/g-mol
x	mole fraction
Z_{RA}	constant in modified Rackett equation

Subscripts

c	ciritical value
i,j	components
ij	i–j binary interaction
m	mixture value
r	reduced value

Literature Cited

(1) Timmermans, J., "Physico-Chemical Constants of Pure Organic Compounds", Elsevier, New York, 1950 and 1965.
(2) Dean, J. A., "Lange's Hand Book of Chemistry", 11th ed, McGraw-Hill, New Delhi, 1973.
(3) "API Technical Data Book, Division of Refining, Petroleum Refining", 2nd ed., American Petroleum Institute, Washington, D.C., 1971.
(4) Vargaftik, N. B., "Tables on Thermophysical Properties of Liquids and Gaes", 2nd ed., Wiley, New York, 1975.
(5) Spencer, C. F., Danner, R. P., *J. Chem. Eng. Data*, **18**, 230 (1973).
(6) Chiu, C. H., Hsi, C., Ruether, J. A., Lu, B. C. Y., *Can. J. Chem. Eng.*, **51**, 751 (1973).
(7) Ritter, R. B., Lenoir, J. M., Schweppe, J. L., *Pet. Refiner*, **37** (11), 225 (1958).
(8) Yen, L. C., Woods, S. S., *AIChE J.*, **12**, 95 (1966).
(9) Harmens, A., *Chem. Eng. Sci.*, **20**, 813 (1965); **21**, 725 (1966).
(10) Rackett, H. G., *J. Chem. Eng. Data*, **16**, 308 (1971).
(11) Phillips, E. M., Thodos, G., *AIChE J.*, **7**, 413 (1961).
(12) Hanson, G. H. et al. *Ind. Eng. Chem.*, **38**, 1161 (1944).
(13) Rackett, H. G., *J. Chem. Eng. Data*, **15**, 514 (1970).
(14) Spencer, C. F., Danner, R. P., *J. Chem. Eng. Data*, **17**, 236 (1972).
(15) Prausnitz, J. M., Chueh, P. L., "Computer Calculations for High Pressure Vapor Liquid Equilibria", Prentice-Hall, Englewood Cliffs, N.J., 1968.
(16) Barner, H. E., Quinlan, C. W., *Ind. Eng. Chem. Process. Des. Develop.*, **8**, 407 (1969).
(17) Lee, B. I., Kesler, M. G., *AIChE J.* **21**, 510 (1975).
(18) Li, C. C., *Can J. Chem. Eng.*, **49**, 709 (1971).
(19) Reid, R. C., Prausnitz, J. M., Sherwood, T. K. "Properties of Gases and Liquids", McGraw-Hill, New York, 1977.
(20) Halm, R. L., Stiel, L. I., *AIChE J.*, **18**, 3 (1970).
(21) Joffe, J., Zudkevitch, D., *AIChE Symp. Ser.*, **70** (no. 140), 22 (1974).
(22) Gunn, R. D., Yamada, T., *AIChE J.*, **17**, 341 (1971).
(23) Spencer, C. F., Adler, S. B., *J. Chem. Eng. Data*, **23**, 82 (1978).
(24) Hankinson, R. W., Thomson, G. H., *AIChE J.*, **25**, 653 (1979).

Received for review May 7, 1979. Accepted January 28, 1980.

Vapor–Liquid Equilibrium Data for the Systems H_2O–H_2SO_4–HCl, H_2O–H_2SO_4–HBr, and H_2O–HBr at 780 mmHg Pressure

Jean-Louis E. Chevalier* and Yves H. Gaston-Bonhomme

Laboratoire de Génie Chimique, Université d'Aix-Marseille III, 13397 Marseille Cedex 4, France

With the help of a dynamic still made of tantalum, the liquid–vapor equilibria in the ternary systems H_2O–H_2SO_4–HCl and H_2O–H_2SO_4–HBr have been determined for the range of concentrations used in extractive distillation with sulfuric acid as solvent. Liquid–vapor equilibrium in the binary system H_2O–HBr has been determined for concentrations lower than that of the azeotrope. Hála's correlation is used to calculate the equilibrium compositions. Equilibrium temperatures are correlated with an empirical relation.

All the measurements found in the literature (*1*, *2*) relating to isobaric liquid–vapor equilibrium of the system H_2O–H_2SO–HCl cover a very small range of low hydrogen acid mole fractions only. For the system H_2O–H_2SO_4–HBr no result has been published at this date.

The importance of the knowledge of phase equilibria, particularly for the design of extractive distillation columns destined to completely recover the hydracid by removing the azeotrope H_2O–HCl or H_2O–HBr in the presence of sulfuric acid as solvent, has involved us in determining liquid–vapor equilibria in the two ternary systems H_2O–H_2SO_4–HBr and H_2O–H_2SO_4–HCl. The equilibrium of the binary H_2O–HBr has been also determined for concentrations lower than that of the azeotrope.

Experimental Method

Liquid–vapor equilibria are realized with the help of a dynamic Aubry-Gilot' pattern still (*3*). It consists of a tantalum coil mounted in a vessel through which circulates a thermoregulated fluid. The investigated solution passes continuously through the tantalum coil at a rate which permits sufficient contact time to establish thermal and phase equilibrium. At the outlet, the liquid

0021-9568/80/1725-0271$01.00/0