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Prediction of vapor-liquid equilibria

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PREDICTION OF VAPOR-LIQUID EQUILIBRIA

BY

DANIEL J. MC HALE, JR.

A THESIS
SUBMITTED TO THE FACULTY OF
THE DEPARTMENT OF CHEMICAL ENGINEERING
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ABSTRACT

Several equations for predicting vapor-liquid equilibria from the physical properties of the components have been proposed in the literature. Two equations of this type proposed by O. Redlich and others have been investigated to determine their utility.

Results indicate the two equations give fairly satisfactory results for nearly ideal solutions, but are unsatisfactory for non-ideal solutions. Knowledge of molecular interactions in the solution would be necessary before the predictions could be used with confidence.

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INTRODUCTION

Knowledge of vapor-liquid equilibria data is essential to derive quantitative relations for many of the more important separation operations of modern industry. However, laboratory determination of vapor-liquid equilibria is not simple. Considerable technique is needed to assure reliable results. As systems increase in complexity and conditions deviate considerably from atmospheric pressure, accuracy decreases and a large number of experiments are necessary to describe a system.

The most logical approach to this difficulty is to collect data under optimum experimental conditions, such as binary systems near atmospheric pressure. Data are then extended to design conditions by thermodynamic analysis. Determination of vapor-liquid equilibria by thermodynamic principles from the physical properties of the pure components would be the ideal arrangement.

Redlich et al (12) have proposed several equations to predict vapor-liquid equilibria of binary systems from the physical properties of the components without resorting to vapor-liquid measurements. However, in several articles co-authored by Redlich, (12, 13) the emphasis has been on checking and smoothing experimental data rather than prediction of vapor-liquid equilibria. A thorough

investigation of the accuracy of the equations has not been published as far as the author is aware.

The purpose of this paper is to check Redlich's equations extensively and to determine the range of utility of the equations. Basically, the method of investigation involved solution of the Redlich equations, conversion of the calculated constants to Margules coefficients, and comparison of the calculated Margules coefficients with literature values for the same binary systems.

THEORY AND DERIVATIONS

The thermodynamic relations of vapor-liquid equilibria are complex and rigorous treatment becomes increasingly difficult as systems deviate from ideal conditions. Simplifying assumptions must be made to treat the data conveniently. Use of these assumptions decreases the effectiveness of thermodynamic analysis, and results are often qualitative rather than quantitative. However, even in the former case, the results are informative in describing the general behavior of the system.

Thermodynamic analysis is most useful if general relationships can be derived from specific experimental data. The general relations then can be applied to a wide range of conditions free from restriction to the original experimental data.

Activity and fugacity coefficients are of particular value as thermodynamic relations in equilibrium problems. These coefficients are basically fundamental properties and have the additional advantage that they may be derived from the conditions of one phase. For example, activity coefficients depend only on the temperature and nature of the liquid phase with the influence of the vapor phase eliminated. (12)

Activity coefficients for binary system are often

expressed in terms of deviations from Raoult's law by the equations: (8)

$$\gamma_1 = \frac{\pi y_1}{P_1 x_1} \quad ; \quad \gamma_2 = \frac{\pi y_2}{P_2 x_2} \quad (1)$$

where

γ_i = activity coefficient of component 1, conventionally the lower boiling component.

π = Total pressure of the system.

x_1 = Mole fraction component 1 in liquid phase.

y_1 = Mole fraction component 1 in vapor phase.

P_1 = Vapor pressure of pure component 1 at the temperature of the system.

The above equations assume that the vapors are ideal gases, which is a very good approximation for systems at or near atmospheric pressure.

Carlson and Colburn (2) used the above equations in combination with the Gibbs-Duhem equation to express activity coefficients at constant temperature as follows:

$$x_1 \left(\frac{\partial \ln \gamma_1}{\partial x_1} \right)_{T, \pi} + x_2 \left(\frac{\partial \ln \gamma_2}{\partial x_2} \right)_{T, \pi} + \dots = 0 \quad (2)$$

For binary mixtures, $\partial x_1 = -\partial x_2$ so,

$$x_1 \left(\frac{\partial \ln \gamma_1}{\partial x_1} \right)_{T, \pi} = x_2 \left(\frac{\partial \ln \gamma_2}{\partial x_2} \right)_{T, \pi} \quad (3)$$

These equations are rigorous for isothermal systems, but may be applied to constant pressure data without serious error. The main field of usefulness, as explained

by Dodge (3) and Carlson and Colburn (2), for this form of the Gibbs-Duhem equation is to give qualitative checks for consistency of vapor-liquid experimental data.

If certain assumptions are made, Equations (2) and (3) may be solved for several special cases. The solutions obtained are helpful in interpreting vapor-liquid equilibrium data. While several investigators (11,14,16) used different approaches to solve the equations, it was pointed out by Wohl (17) that the results derived were special cases of a general equation for excess free energy of solution of two components. Hougen and Watson (8) show the results of Wohl's analysis and its application to previous solutions of the equations.

Wohl's final equations for binary systems are given in the form:

$$\log \gamma_1 = Z_2^2 \left[A + 2 \left(B \frac{q_1}{q_2} - A \right) Z_1 \right] \quad (4)$$

$$\log \gamma_2 = Z_1^2 \left[B + 2 \left(A \frac{q_2}{q_1} - B \right) Z_2 \right] \quad (5)$$

where

Z = Volume fraction based on the volumes of the pure components and is the true volume fraction if volume changes in mixing are negligible.

q = Effective molar volume.

A, B = Constants for conditions of system.

The Wohl solution involves three constants, A, B, and q_1 / q_2 which must be determined empirically for each system. However, if various assumptions are made concerning the ratio q_1 / q_2 , the number of constants to be determined is only two.

Margules' (11) solution of Equations (2) and (3) in effect assumed that the ratio of q_1 / q_2 in Equations (4) and (5) was equal to unity. On this basis, Equations (4) and (5) reduce to the Margules equations as modified by Carlson and Colburn (2):

$$\log \gamma_1 = X_2^2 [A + 2(B-A)X_1] = (2B-A)X_2^2 + 2(A-B)X_2^3 \quad (6)$$

$$\log \gamma_2 = X_1^2 [B + 2(A-B)X_2] = (2A-B)X_1^2 + 2(B-A)X_1^3 \quad (7)$$

If q_1 / q_2 is assumed equal to A/B, Equation (4) and (5) can be expressed as those developed by van Laar (16) and rearranged by Carlson and Colburn (2):

$$\log \gamma_1 = A Z_2^2 = \frac{A X_2^2}{\left(\frac{A}{B} X_1 + X_2\right)^2} \quad (8)$$

$$\log \gamma_2 = B Z_1^2 = \frac{B X_1^2}{\left(X_1 + \frac{B}{A} X_2\right)^2} \quad (9)$$

As Carlson and Colburn (2) pointed out, the equations of Margules and van Laar are equal when $A = B$. When A does not equal B, the two sets of equations represent different curves and the difference is greater as the ratio A/B departs from unity. Literature data are primarily given

as van Laar constants because the van Laar equations seem to represent the majority of experimental data most satisfactorily. However, for the calculations involved in this paper, van Laar constants were used as approximations to Margules constants to facilitate mathematical computations.

The criterion given by Perry (1) that van Laar constants and Margules constants may be used interchangeably in certain cases was adopted. Perry recommended that, for practical purposes, van Laar and Margules constants are similar if the ratio A/B is in the range of about 0.75 to 1.3. Very few systems used in this investigation had values of A/B near those limits. Several systems for which the ratio A/B approached 0.75 or 1.3 were checked by calculating activity coefficients from the van Laar constants at $x_1 = 0.5$, and then calculating the Margules constant. In these cases, differences between van Laar and Margules constants were always less than 3 percent. Hence, the conclusions reached in this investigation for Margules constants apply qualitatively to van Laar constants.

A third relation can be derived from Equations (4) and (5) if the effective molar volumes are assumed equal to the actual molar volumes. This method assumes $q_1 / q_2 = V_1 / V_2$ and Equations (4) and (5) reduce to the Scatchard-

Hamer (14) equations in the form given by Hougén and Watson (8):

$$\log \gamma_1 = Z_2^2 \left[A + 2 \left(B \frac{V_1}{V_2} - A \right) Z_1 \right] \quad (10)$$

$$\log \gamma_2 = Z_1^2 \left[B + 2 \left(A \frac{V_2}{V_1} - B \right) Z_2 \right] \quad (11)$$

where V_1, V_2 are the molar volumes of pure components.

Redlich et al (12) have suggested another method for representing activity coefficients by means of empirical constants. A function Q for a binary system is defined as:

$$Q = X_1 \log \gamma_1 + X_2 \log \gamma_2 \quad (12)$$

The function Q is also defined in terms of empirical constants by:

$$Q = X_1 X_2 \left[b + c (x_1 - x_2) + d (x_1 - x_2)^2 + \dots \right] \quad (13)$$

where the coefficients b, c, d, \dots depend on the temperature. The thermodynamic relations for the activity coefficients are:

$$\log \gamma_1 = Q + X_2 \frac{dQ}{dX_1} \quad ; \quad \log \gamma_2 = Q - X_1 \frac{dQ}{dX_1} \quad (14)$$

so that

$$\log \gamma_1 = X_2^2 \left[b + c (3x_1 - x_2) + d (x_1 - x_2)(5x_1 - x_2) + \dots \right] \quad (15)$$

$$\log \gamma_2 = X_1^2 \left[b + c (x_1 - 3x_2) + d (x_1 - x_2)(x_1 - 5x_2) + \dots \right] \quad (16)$$

Redlich claims these series furnish the most convenient representation of activity coefficients. For a nearly perfect solution, only the first constant b is required. Two terms are sufficient for a non-ideal, non-associated

system. For solutions containing an associated molecule such as an alcohol or an acid, the third term d is necessary. However, for the purposes of this paper and for simplicity in calculation, the third term d was neglected even if an associated molecule were present in the binary system.

Equations (6) of Margules and (15) of Redlich may be readily rearranged in the following form where A_m and B_m indicate the Margules coefficients and only the b and c Redlich coefficients are considered:

$$\frac{\log \delta_1}{x_2^2} = A_m + 2(B_m - A_m)x_1 \quad (17)$$

$$\frac{\log \delta_1}{x_2^2} = b + c(3x_1 - x_2) \quad (18)$$

Substituting $x_2 = 1 - x_1$,

$$\frac{\log \delta_1}{x_2^2} = b + c(4x_1 - 1) \quad (19)$$

Multiplying out and regrouping, Equation (19) becomes:

$$\frac{\log \delta_1}{x_2^2} = (b - c) + 4cx_1 \quad (20)$$

Equating the coefficients of Equations (17) and (20)

$$A_m = b - c \quad (21)$$

$$B_m = b + c \quad (22)$$

Equations (21) and (22) were the basis for the comparisons between experimental and predicted data developed in this investigation. The experimental values for the Margules constants were taken as the van Laar constants given in the literature as explained previously. Cal-

culated values for b and c were derived from the equations suggested by Redlich et al.

A relation expressing activity coefficients in terms of molar volumes and critical properties of the components was developed by van Laar using the van der Waals equation of state. Redlich has approximated the equation as an expression for the coefficient b of Equation (15) and (16):

$$b = 0.4343 (r_1 - r_2)^2 \left[\frac{27 R V_1 V_2}{32 T (V_1 + V_2)} + 4 / (V_1 + V_2)^2 \right] \quad (23)$$

The ratio r_1 is given by the molar volumes of the first component and its critical temperature T_{c1} and critical pressure p_{c1} as follows:

$$r_1 = \frac{T_{c1}}{(p_{c1})^{0.5} V_1} \quad (24)$$

A second equation developed by Scatchard(15) was approximated by Redlich as:

$$b = 0.869 \left[\left(\frac{E_1}{V_1} \right)^{0.5} - \left(\frac{E_2}{V_2} \right)^{0.5} \right]^2 \frac{V_1 V_2}{RT(V_1 + V_2)} \quad (25)$$

where E_1 and E_2 are the molar heats of vaporization minus RT .

Redlich states that in the examples which have been studied, the difference in results by Equations (23) and (25) have hardly been significant.

If the larger of the two component molecules is a chain, an entropy correction must be added according to the theory developed by Huggens (9), and Guggenheim (5). Redlich has approximated the entropy term by the following expression:

$$b = 2 \log_{10} \left[4 v_1 v_2 / (v_1 + v_2)^2 \right] \quad (26)$$

Redlich points out that development of Equations (23) through (26) were based on volume fractions rather than mole fractions. Practically they are good approximations if:

$$2/3 < \frac{v_2}{v_1} < 3/2 \quad (27)$$

Under the same conditions, the coefficient c is given by:

$$c = b (v_2 - v_1) / (v_2 + v_1) \quad (28)$$

Several general conclusions regarding the utility of the equations were given by Redlich. These conclusions are discussed later in the Discussion of Results section.

METHOD OF CALCULATION

Margules constants in the literature were available only for the systems n heptane-toluene, m xylene-aniline, and p xylene-aniline. All other constants used were van Laar constants in the range where van Laar constants and Margules constants are equivalent. If the ratio of the van Laar constants A/B was not in the range 0.70-1.3, the system was rejected.

An average temperature and pressure was calculated from the experimental data in the literature. Molecular volumes at these conditions were calculated. If the ratio of the molecular volumes V_1 / V_2 fell outside the range 0.67-1.50 established by Equation (27), the system was discarded.

Essentially the calculations consisted of substituting the proper data into Equations (23) plus (28) or (25) plus (28). These equations were then solved for the Redlich constants b and c . If the larger molecule was a chain, the entropy correction of Equation (26) was added to the b term.

The calculated values of b and c were converted to Margules coefficients by means of Equations (21) and (22). The percent deviation was then derived from the follow-

ing relation:

$$\% \text{ Deviation} = 100 \left[\frac{\left(\text{Calculated Margules Constant} \right) - \left(\text{Literature Margules Constant} \right)}{\text{Literature Margules Constant}} \right] \quad (29)$$

In calculating percent deviations for the n dodecane-1-octadecene systems which involved negative coefficients, a slightly altered procedure was used. Only the absolute value of the literature constant without regard to sign was used in the denominator of Equation (29). In effect, this establishes a numerical system running from minus infinity to plus infinity. Under this system, a small negative number has a larger positive value than a large negative number. This procedure was necessary to maintain consistency because the calculated Margules constants were sometimes negative and sometimes positive.

Molecular volumes required for the calculations were derived from three sources. Literature values or values calculated readily from literature sources were used where possible. As a second resort, densities were calculated by the method of Hanson (6). Briefly Hanson's method consisted of finding reduced volumes from the reduced temperatures involved and calculating the desired density by the relation:

$$D = \frac{V_{R_1}}{V_R} D_1 \quad (30)$$

A reproduction of the reduced temperature-reduced volume chart developed by Hanson is shown as Figure 1 in the Appendix. When Hanson's method could not be applied, the familiar method of Hougen and Watson (8) was used, where:

$$V = \frac{V_1 \omega_1}{\omega} \quad (31)$$

where ω is a function of reduced temperature and reduced pressure.

Molar heat of vaporization data was usually available in the literature at the normal boiling point. Conversion of heat of vaporization data to other temperatures was accomplished by the equation of Hougen and Watson (7):

$$\frac{\lambda}{\lambda_1} = \left(\frac{1 - T_R}{1 - T_{R_1}} \right)^{0.38} \quad (32)$$

Critical properties required were taken from the literature in most cases. However, the critical properties of 1-octadecene were estimated, due to lack of published data, by the method of Gamson and Watson (4). Heat of vaporization for this compound was estimated by the Kistya-kowsky equation given in Hougen and Watson (7).

RESULTS

Comparison of literature and predicted Margules constants is made in Tables 1 through 4 on the following pages. Tables 1 and 2 show the results calculated by Equations (23), (26), and (28). These equations are based on critical properties and molar volumes. Tables 3 and 4 list the results based on Equations (25), (26), and (28) which require heat of vaporization and molar volume data.

For clarity, the average temperature and pressure of each system has been shown in Table 1 and omitted from Tables 2,3, and 4. The conditions noted in Table 1 for a given system apply to the same numbered system in Tables 2,3,and 4. This procedure has been followed in all additional tables relating to specific systems.

TABLE 1Literature and Predicted¹ Margules Constant, A_m

System and Reference	T °C	P_r Atms.	Margules Constant, A_m		
			Lit.	Calc.	% Devi- ation
1. Acetone-Benzene (1)	68.0	1.00	0.176	0.008	-95.0
2. n Butanol-n Butyl Acetate (1)	121.6	1.00	0.22	0.471	114.0
3. n Butane-Furfural (6)	37.8	2.24	1.096	1.036	-6.0
4. n Butane-Furfural (6)	51.7	3.04	1.045	0.954	-8.7
5. n Butane-Furfural (6)	66.6	4.36	0.998	1.040	5.2
6. n Butane-Furfural (6)	93.3	3.76	0.908	1.194	31.5
7. 1-Butene-Furfrual (6)	37.8	2.40	0.842	0.940	11.6
8. 1-Butene-Furfural (6)	51.7	3.03	0.800	0.817	2.1
9. 1-Butene-Furfural (6)	66.6	4.39	0.763	0.941	23.4
10. 1-Butene-Furfural (6)	93.3	3.76	0.700	1.101	57.2
11. Carbon Disulfide- Acetone (1)	51.0	1.00	0.556	0.004	-95.5
12. Carbon Tetrachlor- ide-Benzene (1)	78.0	1.00	0.052	0.021	-59.8
13. n Dodecane-1-Octa- decene (4)	268.0	1.00	-0.187	-0.010	94.5
14. n Dodecane-1-Octa- decene (4)	240.0	0.53	-0.166	-0.011	93.5
15. n Dodecane-1-Octa- decene (4)	211.0	0.25	-0.137	-0.011	92.0
16. n Dodecane-1-Octa- decene (4)	168.0	0.006	-0.097	-0.012	87.5

¹ From critical properties and molar volumes.

TABLE 1 (CONTINUED)Literature and Predicted Margules Constant, Am

System and Reference	T	p	Margules Constant, Am		
	°C	Atms.	Lit.	Calc.	% Devi- ation
17. Ethyl Acetate-Benzene (1)	75.6	1.00	0.50	0.025	-94.9
18. Ethyl Alcohol-Benzene (1)	74.0	1.00	0.845	0.086	-89.8
19. Ethyl Alcohol-Trichloroethylene (1)	78.5	1.00	0.845	0.138	-83.7
20. Ethyl Ether-Acetone (1)	45.3	1.00	0.322	0.293	-9.0
21. n Heptane-Toluene (3)	104.5	1.00	0.022	0.203	825.0
22. Isobutane-Furfural (6)	37.8	2.71	1.142	1.234	8.1
23. Isobutane-Furfural (6)	51.7	4.40	1.090	1.198	9.9
24. Isobutane-Furfural (6)	66.6	4.75	1.042	1.332	27.8
25. Isobutane-Furfural (6)	93.3	5.27	0.955	1.557	63.0
26. Methylcyclohexane-Toluene (7)	105.0	1.00	1.19	0.258	-78.2
27. Methylcyclohexane-Toluene (7)	84.6	0.53	1.28	0.265	-79.4
28. Methylcyclohexane-Toluene (7)	64.5	0.26	1.55	0.252	-83.6
29. Propane-Propylene (2)	-14.0	4.68	0.024	0.165	588.0
30. m Xylene-Aniline (5)	160.5	0.98	0.520	0.238	-54.2
31. p Xylene-Aniline (5)	155.5	0.98	0.400	0.230	-42.5

1 From critical properties and molar volumes.

TABLE 2Literature and Predicted¹ Margules Constant, Bm

System	Margules Constant, Bm		
	Literature	Calculated	% Deviation
1. Acetone-Benzene	0.176	0.009	-95.0
2. n Butanol-n-Butyl Acetate	0.24	0.857	257.0
3. n Butane-Furfural	1.257	0.838	-41.9
4. n Butane-Furfural	1.171	0.762	-34.9
5. n Butane-Furfural	1.108	0.812	-26.7
6. n Butane-Furfural	0.975	0.876	-10.1
7. 1-Butene-Furfural	1.029	0.780	-24.2
8. 1-Butene-Furfural	0.986	0.683	-30.8
9. 1-Butene-Furfural	0.951	0.769	-19.1
10. 1-Butene-Furfural	0.900	0.841	-6.6
11. Carbon Disulfide- Acetone	0.778	0.005	-95.5
12. Carbon Tetrachlor- ide-Benzene	0.046	0.023	-49.3
13. n Dodecane-1-Octa- decene	-0.258	-0.012	95.5
14. n Dodecane-1-Octa- decene	-0.220	-0.015	93.1
15. n Dodecane-1-Octa- decene	-0.204	-0.014	92.1
16. n Dodecane-1-Octa- decene	-0.146	-0.015	89.9

¹ From critical properties and molar volumes.

TABLE 2(CONTINUED)Literature and Predicted¹ Margules Constant, Bm

System	Margules Constant, Bm		
	Literature	Calculated	% Deviation
17. Ethyl Acetate-Benzene	0.40	0.025	-93.7
18. Ethyl Alcohol-Benzene	0.699	0.128	-81.8
19. Ethyl Alcohol-Trichloroethylene	0.653	0.214	-67.2
20. Ethyl Ether-Acetone	0.322	0.209	-35.1
21. n Heptane-Toluene	0.133	0.143	7.5
22. Isobutane-Furfural	1.310	0.960	-26.7
23. Isobutane-Furfural	1.213	0.914	-24.6
24. Isobutane-Furfural	1.160	0.988	-14.8
25. Isobutane-Furfural	1.030	1.063	3.2
26. Methylcyclohexane-Toluene	1.21	0.210	-82.6
27. Methylcyclohexane-Toluene	1.23	0.217	-82.6
28. Methylcyclohexane-Toluene	1.33	0.213	-83.9
29. Propane-Propylene	0.033	0.143	333.0
30. m Xylene-Aniline	0.245	0.170	-30.6
31. p Xylene-Aniline	0.493	0.164	-66.7

1 From Critical properties and molar volumes.

TABLE 3Literature and Predicted¹ Margules Constant, Am

System	Margules Constant, Am		
	Literature	Calculated	% Deviation
1. Acetone-Benzene	0.176	0.007	-95.5
2. n Butanol-n Butyl Acetate	0.22	0.333	51.3
3. n Butane-Furfrual	1.096	1.283	17.0
4. n Butane-Furfural	1.045	1.604	53.5
5. n Butane-Furfural	0.998	1.684	68.7
6. n Butane-Furfural	0.908	2.008	121.0
7. 1-Butene-Furfural	0.842	1.483	76.3
8. 1-Butene-Furfural	0.800	1.552	94.0
9. 1-Butene-Furfural	0.763	1.629	113.5
10. 1-Butene-Furfural	0.700	1.983	169.0
11. Carbon Disulfide- Acetone	0.556	0.002	-99.4
12. Carbon Tetrachlor- ide-Benzene	0.052	0.020	-57.7
13. n Dodecane-1-Octa- decene	-0.187	0.113	160.0
14. n Dodecane-1-Octa- decene	-0.166	0.080	148.0
15. n Dodecane-1-Octa- decene	-0.137	0.078	157.0
16. n Dodecane-1-Octa- decene	-0.097	0.050	152.0

¹ From heats of vaporization and molar volumes.

TABLE 3 (CONTINUED)Literature and Predicted¹ Margules Constant, Am

System	Margules Constant, Am		
	Literature	Calculated	% Deviation
17. Ethyl Acetate-Benzene	0.50	0.023	-95.4
18. Ethyl Alcohol-Benzene	0.845	0.429	-49.2
19. Ethyl Alcohol-Trichloroethylene	0.845	0.424	-49.8
20. Ethyl Ether-Acetone	0.322	0.346	7.5
21. n Heptane-Toluene	0.022	0.218	891.0
22. Isobutane-Furfural	1.142	1.995	74.7
23. Isobutane-Furfural	1.090	2.041	87.2
24. Isobutane-Furfural	1.042	2.163	107.0
25. Isobutane-Furfural	0.955	2.680	170.0
26. Methylcyclohexane-Toluene	1.19	0.170	-85.5
27. Methylcyclohexane-Toluene	1.28	0.152	-88.2
28. Methylcyclohexane-Toluene	1.55	0.161	-89.7
29. Propane-Propylene	0.024	0.0002	-99.1
30. m Xylene-Aniline	0.520	0.443	-14.8
31. p Xylene-Aniline	0.400	0.453	13.2

¹ From heats of vaporization and molar volumes.

TABLE 4Literature and Predicted¹ Margules Constant, Bm

System	Margules Constant, Bm		
	Literature	Calculated	% Deviation
1. Acetone-Benzene	0.176	0.008	-95.0
2. n Butanol-n Butyl Acetate	0.24	0.499	108.0
3. n Butane-Furfural	1.257	1.043	-16.9
4. n Butane-Furfural	1.171	1.280	9.3
5. n Butane-Furfural	1.108	1.316	18.8
6. n Butane-Furfural	0.975	1.472	51.0
7. 1-Butene-Furfural	1.029	1.263	22.8
8. 1-Butene-Furfural	0.986	1.298	31.7
9. 1-Butene-Furfural	0.951	1.331	40.0
10. 1-Butene-Furfural	0.900	1.517	68.5
11. Carbon Disulfide- Acetone	0.778	0.003	-99.6
12. Carbon Tetrachlor- ide-Benzene	0.046	0.022	-51.4
13. n Dodecane-1-Octa- decene	-0.258	0.141	154.0
14. n Dodecane-1-Octa- decene	-0.220	0.102	146.0
15. n Dodecane-1-Octa- decene	-0.204	0.100	149.0
16. n Dodecane-1-Octa- decene	-0.246	0.066	145.0

¹ From heats of vaporization and molar volumes.

TABLE 4 (CONTINUED)

<u>Literature and Predicted¹ Margules Constant, Bm</u>			
System	Margules Constant, Bm		
	Literature	Calculated	% Deviation
17. Ethyl Acetate-Benzene	0.40	0.023	-94.3
18. Ethyl Alcohol-Benzene	0.699	0.641	-9.0
19. Ethyl Alcohol-Trichloroethylene	0.653	0.658	0.8
20. Ethyl Ether-Acetone	0.322	0.246	-23.6
21. n Heptane-Toluene	0.133	0.154	15.8
22. Isobutane-Furfural	1.310	1.549	18.9
23. Isobutane-Furfural	1.213	1.559	28.2
24. Isobutane-Furfural	1.160	1.607	42.7
25. Isobutane-Furfural	1.030	1.830	77.7
26. Methylcyclohexane-Toluene	1.21	0.139	-88.3
27. Methylcyclohexane-Toluene	1.23	0.124	-89.9
28. Methylcyclohexane-Toluene	1.33	0.133	-89.9
29. Propane-Propylene	0.033	0.0002	-99.3
30. m Xylene-Aniline	0.245	0.317	29.4
31. p Xylene-Aniline	0.493	0.323	-34.5

¹ From heats of vaporization and molar volumes.

DISCUSSION OF RESULTS

The data in Tables 1 through 4 were analyzed in terms of the percent deviation of predicted Margules constants from literature Margules constants. A breakdown of the significant data in Tables 1 through 4 into two additional tables is shown on the next two pages. Table 5 lists those systems for which the percent deviations of literature and predicted Margules constants were below 80 percent. Only those systems for which it was possible, within the specified deviation, to calculate both Margules constants A_m and B_m by either or both of the proposed methods were considered. Table 6 lists those systems for which the maximum deviation between literature and predicted Margules constants was below 40 percent.

The criterion of 40 percent maximum deviation as an indication of fairly good agreement has been arbitrarily selected. Redlich (12) shows a graph comparing calculated and experimental values for the constant b of Equations (23) and (25) for mixtures of normal paraffins in benzene. Points have been selected from this graph in the present study and the percent deviation of predicted and experimental values determined for comparison with results of the present study.

The deviations ranged from -16.6 to 60.0 percent with

TABLE 5

Systems For Which Percent Deviation Between Literature
And Predicted Margules Constants Is Below 80 Maximum

System	% Deviation			
	Tables 1,2		Tables 3,4	
	A _m	B _m	A _m	B _m
3. n Butane-Furfural	-6.0	-41.9	17.0	-16.9
4. n Butane-Furfural	-8.7	-34.9	53.5	9.3
5. n Butane-Furfural	5.2	-26.7	68.7	18.8
6. n Butane-Furfural	31.5	-10.1	--	51.0
7. 1-Butene-Furfural	11.6	-24.2	76.3	22.8
8. 1-Butene-Furfural	2.1	-30.8	--	31.7
9. 1-Butene-Furfural	23.4	-19.1	--	40.0
10. 1-Butene-Furfural	57.2	-6.6	--	68.5
12. Carbon Tetrachloride- Benzene	-59.8	-49.3	-57.7	-51.4
18. Ethyl Alcohol-Benzene	--	--	-49.2	-9.0
19. Ethyl Alcohol-Tri- chloroethylene	--	-67.2	-49.8	0.8
20. Ethyl Ether-Acetone	-9.0	-35.1	7.5	-23.6
22. Isobutane-Furfural	8.1	-26.7	74.7	18.9
23. Isobutane-Furfural	9.9	-24.6	--	28.2
24. Isobutane-Furfural	27.8	-14.8	--	42.7
25. Isobutane-Furfural	63.0	3.2	--	77.7
30. m Xylene-Aniline	-54.2	-30.6	-14.8	29.4
31. p Xylene-Aniline	-42.5	-66.7	13.2	-34.5

Note: Dash indicates deviation above 80 percent.

TABLE 6

Systems For Which Percent Deviation Between Literature
And Predicted Margules Constants Is Below 40 Maximum

System	% Deviation			
	Tables 1,2		Tables 3,4	
	A _m	B _m	A _m	B _m
3. n Butane-Furfural	-6.0	--	17.0	-16.9
4. n Butane-Furfural	-8.7	-34.9	--	9.3
5. n Butane-Furfural	5.2	-26.7	--	18.8
6. n Butane-Furfural	31.5	-10.1	--	--
7. 1-Butene-Furfural	11.6	-24.2	--	22.8
8. 1-Butene-Furfural	2.1	-30.8	--	31.7
9. 1-Butene-Furfural	23.4	-19.1	--	40.0
20. Ethyl Ether-Acetone	-9.0	-35.1	7.5	-23.6
22. Isobutane-Furfural	8.1	-26.7	--	18.9
23. Isobutane-Furfural	9.9	-24.6	--	28.2
24. Isobutane-Furfural	27.8	-14.8	--	--
30. m Xylene-Aniline	--	-30.6	-14.8	29.4
31. p Xylene-Aniline	--	--	13.2	-34.5

Note: Dash indicates deviation above 40 percent.

an average deviation of 19 percent. Redlich stated that these results were satisfactory, but that comparable results may not be secured for other components. His conclusion appears to be consistent with the results obtained in the present work.

Inspection of Tables 5 and 6 indicates that the methods proposed by Redlich give fairly satisfactory results for approximately 40 percent of the systems studied and qualitative results for an additional 15 percent of the systems.

In the case of those components dissolved in furfural, the agreement is quite good, particularly for values of A_m calculated from critical properties and molar volumes. However, it is felt that the magnitude of the deviations generally restricts the use of the predictions to estimating order of magnitudes of Margules and van Laar constants.

Redlich (12) has stated that the differences in results obtained from Equation (23) involving critical properties and molar volumes, and Equation (25) involving heats of vaporization and molar volumes, have hardly been significant in the examples he has studied. In the present investigation, that relation has held approximately for only six systems: acetone-benzene, carbon disulfide-acetone, carbon tetrachloride-benzene, ethyl acetate-benzene, ethyl ether-acetone, and n heptane-toluene. In four cases,

results predicted by Equation (23) were higher than those predicted by Equation (25). However, in the majority of systems studied, the results from Equation (23) were significantly lower than the results from Equation (25).

As shown in Table 6, satisfactory agreement between literature and predicted values was most often derived by the use of Equation (23). In addition, Equation (23) predicted qualitatively that the n dodecane-1-octadecene systems would have negative constants. Jordan and Van Winkle (10) who investigated the n dodecane-1-octadecene system noted that negative coefficients were unusual for this type system and unexplainable.

In general, the systems which did not give satisfactory agreement contained an associated molecule, an unsymmetrical molecule, or consisted of a paraffin-olefin. The simplifying assumptions necessary to express Redlich's equations in terms of Margules coefficients probably were not justified in these cases. Apparently, the weakness of the prediction methods is that the results cannot be used confidently without some knowledge of molecular interactions of the solution.

CONCLUSIONS

1- Equations proposed by Redlich (12) for prediction of binary vapor-liquid equilibria have been found to give fairly satisfactory results for several systems. No general or common factors were apparent among these systems.

2- An arbitrary criterion of 40 percent maximum deviation between literature Margules constants and predicted Margules constants was adopted. Approximately 40 percent of the systems studied gave satisfactory agreement.

3- The proposed equation involving critical properties and molar volumes was found to give better results for the systems studied than the proposed equation involving heats of vaporization and molar volumes. Redlich did not find significant differences between results of the two equations for the systems he evaluated.

4- In general, systems containing an associated molecule, an unsymmetrical molecule, or a paraffin-olefin combination did not give satisfactory agreement.

5- The proposed Redlich equations are useful mainly as a qualitative prediction method to indicate the order of magnitude of Margules or van Laar constants. The weakness of the equations is that some knowledge of molecular interactions in the solution must be available before the predictions can be used with confidence.

APPENDIX

TABULATED CALCULATIONSEquations (23), (26), and (28)

System	V ₁ ml/mole	V ₂ ml/mole	r ₁	r ₂	b	c
1.	79.3	92.0	0.925	0.880	0.0086	0.0006
2.	100.5	150.0	0.802	0.684	0.714	0.143
3.	103.9	84.0	0.660	1.091	0.937	-0.10
4.	107.2	85.6	0.647	1.060	0.858	-0.096
5.	111.1	86.7	0.624	1.058	0.926	-0.114
6.	121.1	88.9	0.571	1.031	1.035	-0.159
7.	98.7	84.0	0.674	1.091	0.860	-0.08
8.	102.3	85.6	0.660	1.060	0.750	-0.067
9.	106.2	86.7	0.637	1.058	0.885	-0.086
10.	116.6	88.9	0.581	1.031	0.971	-0.133
11.	62.5	77.0	1.000	0.964	0.005	0.0005
12.	103.9	93.0	0.800	0.868	0.022	0.001
13.	320.0	398.0	0.486	0.495	-0.011	-0.001
14.	305.0	393.0	0.510	0.502	-0.013	-0.002
15.	291.0	379.0	0.536	0.519	-0.013	-0.002
16.	276.0	374.0	0.566	0.541	-0.013	-0.002

TABULATED CALCULATIONSEquations (23), (26), and (28) (Continued)

System	V_1 ml/mole	V_2 ml/mole	r_1	r_2	b	c
17.	106.3	92.9	0.800	0.872	0.025	-0.002
18.	62.2	92.9	1.042	0.872	0.107	0.021
19.	62.6	97.0	1.037	0.797	0.176	0.038
20.	107.2	76.3	0.730	0.968	0.251	-0.042
21.	166.0	117.0	0.626	0.803	0.173	-0.030
22.	108.1	84.0	0.630	1.091	1.097	-0.137
23.	112.1	85.6	0.606	1.060	1.056	-0.142
24.	116.9	86.7	0.583	1.058	1.160	-0.172
25.	130.2	88.9	0.523	1.031	1.310	-0.247
26.	145.0	118.0	0.600	0.797	0.234	-0.024
27.	139.0	114.0	0.626	0.825	0.241	-0.024
28.	135.0	111.5	0.646	0.842	0.235	-0.022
29.	80.6	75.8	0.708	0.543	0.154	-0.011
30.	144.0	103.0	0.726	0.932	0.204	-0.034
31.	144.0	102.8	0.735	0.939	0.197	-0.033

TABULATED CALCULATIONSEquations (25), (26), and (28)

System	V ₁ ml/mole	V ₂ ml/mole	E ₁	E ₂	b	c
1.	79.3	92.0	6,400	6,840	0.008	0.0006
2.	100.5	150.0	9,675	7,795	0.416	0.083
3.	103.9	84.0	4,220	10,230	1.160	-0.123
4.	107.2	85.6	3,945	10,015	1.442	-0.162
5.	111.1	86.7	3,660	9,785	1.500	-0.184
6.	121.1	88.9	3,020	9,400	1.740	-0.268
7.	98.7	84.0	4,040	10,230	1.373	-0.110
8.	102.3	85.6	3,725	10,015	1.424	-0.127
9.	106.2	86.7	3,475	9,785	1.480	-0.149
10.	116.6	88.9	2,800	9,400	1.750	-0.233
11.	62.5	77.0	5,725	6,775	0.003	0.0003
12.	103.9	93.0	6,445	6,665	0.0212	0.017
13.	320.0	398.0	7,050	12,830	0.127	0.014
14.	305.0	393.0	7,760	13,680	0.090	0.011
15.	291.0	379.0	8,290	14,440	0.089	0.011
16.	276.0	374.0	9,375	15,500	0.058	0.008

TABULATED CALCULATIONSEquations (25), (26), and (28) (Continued)

System	V ₁ ml/mole	V ₂ ml/mole	E ₁	E ₂	b	c
17.	106.3	92.9	6,955	7,410	0.023	-0.002
18.	62.2	92.9	8,770	6,720	0.535	0.106
19.	62.6	97.0	8,780	7,050	0.541	0.117
20.	107.2	76.3	5,515	6,785	0.296	-0.050
21.	166.0	117.0	6,650	7,420	0.186	-0.032
22.	108.1	84.0	3,730	10,230	1.772	-0.223
23.	112.1	85.6	3,465	10,015	1.800	-0.241
24.	116.9	86.7	3,135	9,785	1.885	-0.278
25.	130.2	88.9	2,430	9,400	2.355	-0.425
26.	145.0	118.0	6,070	7,390	0.155	-0.016
27.	139.0	114.0	6,450	7,600	0.138	-0.014
28.	135.0	111.5	6,775	7,925	0.147	-0.014
29.	80.6	75.8	3,605	3,445	0.0002	N11
30.	144.0	103.0	7,490	9,740	0.380	-0.063
31.	144.0	102.8	7,500	10,600	0.388	-0.065

REDUCED LIQUID VOLUME AS A FUNCTION OF TEMPERATURE

GROUP 1

- Aliphatic Halides
- Aliphatic Mercaptans
- Mono-nuclear Aromatic Hydrocarbons
- Mono-nuclear Aromatic Halides
- Cycloparaffinic Hydrocarbons
- Nitrogen Heterocyclics

GROUP 2

- Amines (C₄ and higher)
- Aliphatic Ethers (C₄ and higher)
- Esters of mono-carboxylic acids
- Phenols

GROUP 3

- Aliphatic Sulfides (C₄ and higher)
- Fatty Acids (C₄ and higher)
- Ketones

GROUP 4

- Alcohols (C₂ and higher)

GROUP 5

- Nitriles

REDUCED LIQUID VOLUME, V_R

0.6

0.5

0.4

0.3

REDUCED TEMPERATURE, T_R

0.5

0.6

0.7

0.8

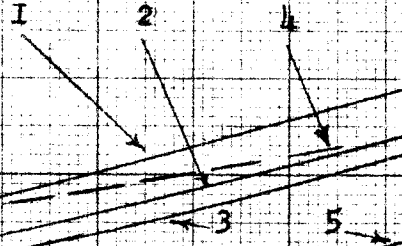
0.9

1.0

Reference: Hanson, E.S., Ind. Eng. Chem., Jan. 1949, Pg. 96-99.

FIGURE 1

35



NOMENCLATURE

A,B	Coefficients of vapor-liquid empirical equations.
b,c	Coefficients of proposed Redlich equations.
E	Heat of vaporization minus RT.
P	Vapor pressure of pure component.
p	Pressure of system, atms.
Q	Redlich function defined by liquid mole fractions. and activity coefficients.
R	Gas Constant.
r	Ratio defined by critical properties and molar volumes.
T	Temperature, °K.
V	Molar volume, ml/mole.
x	Mole fraction in liquid.
y	Mole fraction in vapor.
γ	Activity coefficient.
ω	Expansion factor for liquids.
λ	Heat of vaporization, cal./mole.
π	Total pressure of system.

Subscripts

l	Lower boiling component.
c	Critical property.
m	Margules.
R	Reduced property.

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