Prediction of Vapor-Liquid Equilibrium for Polar-Nonpolar Binary Systems

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This paper presents a method of calculating the van Laar constants for binary vapor-liquid systems. The basis of the method is the van Arkel modification of the van Laar (Scatchard-Hildebrand) equations which utilize the concept of internal pressure. A generalized method of predicting the apparent internal pressure was developed and described. The experimental van Laar constants and those calculated by the proposed method are compared for twelve polar-nonpolar binary systems.

The Scatchard-Hildebrand (*9, 12, 19*) theory of binary solutions has been reasonably successful as a basis in predicting the vapor-liquid equilibria for nonpolar binary systems from the properties of the pure components. However this basis has proved to be unsatisfactory in predicting quantitatively vapor-liquid equilibria for either polar-polar or polar-nonpolar binary systems. Van Arkel (*22, 23*) proposed a model which includes consideration of the effect of polar properties of molecules upon binary vapor-liquid equilibrium data. Hildebrand and Scott (*9*), and more recently Prausnitz and Anderson (*14*), have pointed out that van Arkel's theory has never been tested for binary liquid solutions.

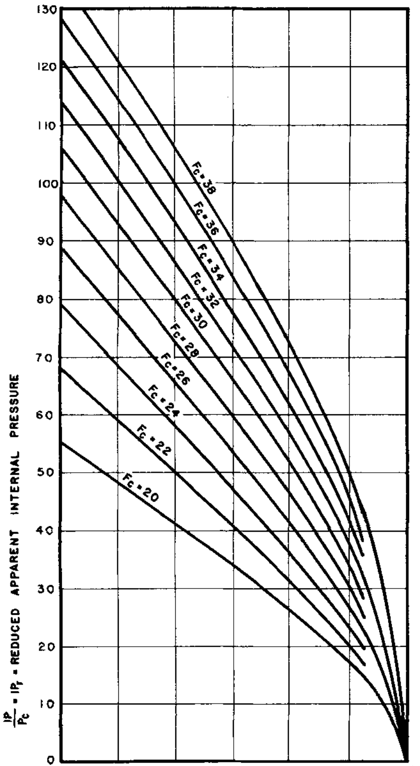

Fig. 1. Reduced apparent internal pressure vs. reduced temperature with parameter F_c smoothed by least squares.

It is the purpose of this paper to present a test of the van Arkel theory for polar-nonpolar binary liquid solutions and to extend this theory empirically where necessary to enable prediction of vapor-liquid equilibrium data from pure component properties.

THEORY

The van Laar Equation (*24*) for binary liquid solutions serves as a basis for the method of calculation. Originally van Laar used the van der Waal equation of state in the development of his equations. Later he and Lorentz (*25*) replaced the van der Waal's covolume *b* with the actual saturated liquid volume V_{L_i}. Scatchard and Hildebrand (*9*) subsequently showed that the concept of internal pressure or cohesive energy density could be incorporated into the van Laar type of equation, and this effectively eliminated the necessity to use van der Waal's assumptions. The theoretical equations of Scatchard-Hildebrand are as follows:

$$\ln \gamma_i = \frac{V_{L_i}(\delta_i - \delta_j)^2 \phi_j^2}{RT} \qquad (1)$$

(Interchange indices $i \neq j$ for γ_j equation.)

Equation (1) has been tested for a large number of systems (*3, 9*) and has been used successfully in describing the behavior of binary solutions containing two nonpolar components. The equation has limited application in describing behavior of binary systems containing polar components. To increase the applicability of the equations to systems containing polar components van Arkel (*22, 23*) proposed that the contribution of the polar properties of a molecule to its internal pressure must be considered.

The theory of van der Waal's dispersion, induction, and orientation forces is well known (*8, 9, 12*), and the relationship between these cohesion forces and the apparent internal pressure is shown in mathematical form as follows:

$$\left[\frac{\Delta E_v}{V_L}\right]_i = \left(\frac{K_s}{V_L}\right)_i^2 \left[\frac{3}{4}\alpha_i^2 h\nu_i + 2\alpha_i \mu_i^2 + \frac{2}{3}\frac{\mu_i^4}{kT}\right] \qquad (2)$$

London demonstrated that the induction term of Equation (2) is always negligible compared with the dispersion and orientation forces for pure compounds (always less than 6% of the total and usually much less). Van Arkel noted that for liquid mixtures the induction forces are generally negligible (*22*). Therefore the authors have defined the dispersion and orien-

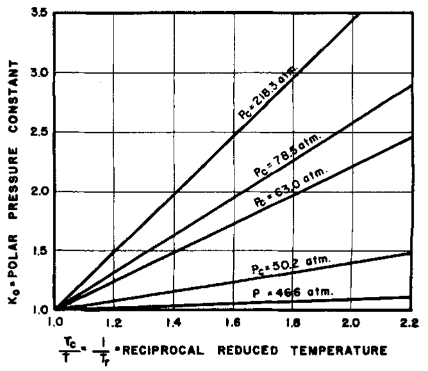

Fig. 2. Polar pressure constant vs. reciprocal reduced temperature with parameter of critical pressure, P_c.

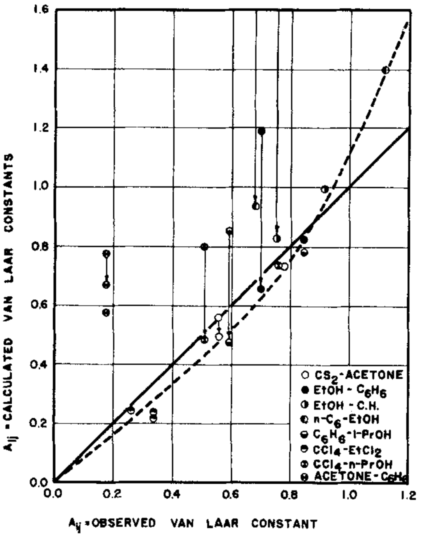

Fig. 3. Calculated vs. observed Van Laar constants as calculated by the van Arkel equations before and after asymmetry modification.

tation parts of Equation (2) as follows:

$$\left[\frac{\Delta E_v}{V_L}\right]_i = \delta_i^2 + \omega_i^2 \qquad (3)$$

where

$$\delta_i^2 = \left[\left(\frac{K_s}{V_L}\right)_i \left(\frac{3}{4}\alpha_i^2 h\nu_i\right)\right] =$$

nonpolar pressure (dispersion) (4*a*)

$$\omega_i^2 = \left[\left(\frac{K_s}{V_L}\right)_i^2 \left(\frac{2}{3}\frac{\mu_i^4}{kT}\right)\right] =$$

polar pressure (orientation) (4*b*)

Thus for a nonpolar molecule ω_i is zero, and the square root of the apparent internal pressure is equivalent to Hildebrand's solubility parameter.

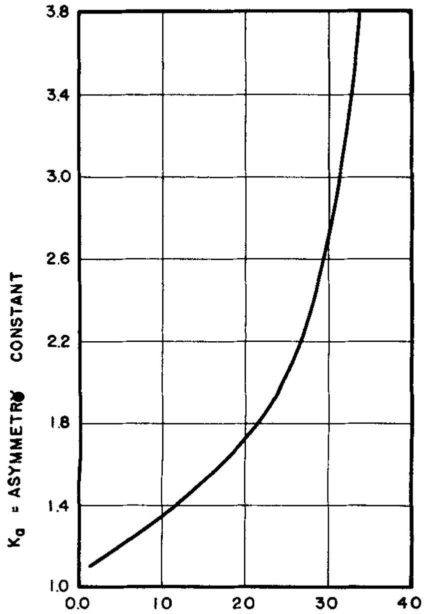

Fig. 4. Asymmetry constant vs. the absolute difference in the square root of apparent internal pressure.

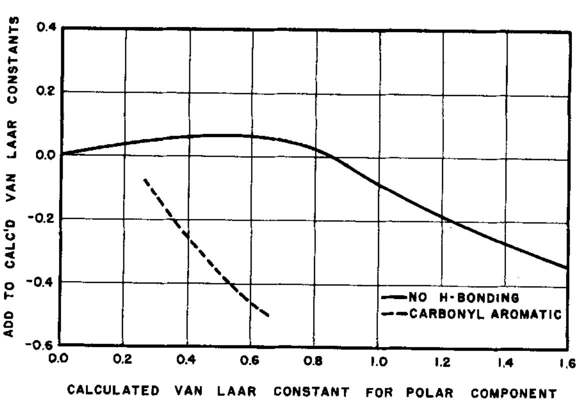

Fig. 5. Final correction factor curve.

If it is assumed that in a liquid mixture the molecules are randomly distributed and are under the influence of spherical force fields, Equation (4) may be used to express the apparent internal pressure of a binary mixture in terms of the individual component polar and nonpolar pressures. As Hildebrand (9) points out, polar molecules do not conform to these requirements, and therefore Equation (4) is an approximate expression.

The Scatchard-Hildebrand type of equation is resolved into Equation (5) when the internal pressure is separated into its polar and nonpolar contributions:

$$\ln \gamma_i = \frac{V_{L_i}[(\delta_i - \delta_j)^2 + (\omega_i - \omega_j)^2]\phi_j^2}{RT} \qquad (5)$$

The limit of Equation (5) may be evaluated to determine the Carlson and Colburn (3) modified van Laar nonideality constant:

$$\underset{\phi_i \to 0}{\text{Lim}} \log \gamma_i = A_{ij} = \frac{V_{L_i}[(\delta_i - \delta_j)^2 + (\omega_i - \omega_j)^2]}{2.303\, RT_j} \qquad (6)$$

Equation (6) is the basic equation used in this study. All quantities in Equation (6) are evaluated at T_j.

APPARENT INTERNAL PRESSURE CORRELATION

In order to use Equation (6) to predict activity coefficients a method of evaluating the apparent internal pressure and its polar and nonpolar contributions was needed. By using a combination of a basic thermodynamic equation and the Clapeyron equation, Equation (7) was derived in which apparent internal pressure (or cohesive energy density), vapor pressure, temperature, and molar volume of vapor and liquid are related:

$$IP = \left[\frac{\Delta E_v}{V_L}\right] = P\left[\left(\frac{d\ln P}{d\ln T}\right) - 1\right]\left[\frac{V_g}{V_L} - 1\right] \qquad (7)$$

The quantities P and $(d\ln P)/(d\ln T)$ have been correlated by Riedel (*18*) by means of the theorem of corresponding states. Riedel's independent variables were reduced temperature and α_c, the value of $(d\ln P)/(d\ln T)$ at the critical point. The quantities V_g and V_L have been correlated by Lyderson et al. (*10*) on the basis of the theorem of corresponding states. Lyderson's independent variables were reduced temperature and the critical compressibility factor. Therefore it was assumed that a correlation of the following form

$$\frac{IP}{P_c} = IP_r = f(T_r, \alpha_c\ Z_c) \qquad (8)$$

should be valid.

Thermodynamic data for seventeen compounds were used to test this hypothesis. It was found that only two independent variables were necessary, that is reduced temperature and the ratio of α_c to Z_c. This ratio is designated as F_c. Although both α_c and Z_c alone were considered as third parameters, only the ratio F_c would yield unique curves with a single parameter.

The reduced apparent internal pressure correlation was fitted by means of least squares to the empirical equation:

$$IP_r^2 = b_p\,(1 - T_r) + c_p\,(1 - T_r)^2 \qquad T_r < 1.0 \quad (9)$$

where

$$b_p = 17{,}559 - 1{,}743.4\, F_c + 49.676\, F_c^2 \qquad (10a)$$

$$c_p = -\,61{,}206 + 4{,}755.0\, F_c - 74{,}206\, F_c^2 \qquad (10b)$$

An IBM-650 computer was used for these calculations. The maximum deviation of the least-squares equations from the data for the seventeen compounds was 3.2%, while the average deviation was less than 1.0%. The least-squares equations are shown graphically in Figure 1.

This generalized correlation was developed because of the scarcity of published apparent internal pressure data, especially data for polar compounds.

POLAR INTERNAL PRESSURE CORRELATION

In order to separate the apparent internal pressure into its polar and nonpolar contributions, Equation (2) was used to evaluate K_s for seventeen nonpolar and nine polar compounds. The left-hand side of Equation (2) was evaluated with molecular constants. The values of K_s varied from 0.71 to 0.83 for the nonpolar compounds, but K_s for the polar compounds varied from 0.47 to 0.96. The results indicated Hildebrand's suggested average value (*9*) of 0.77 for nonpolar compounds to be reasonable but indicated that an average for polar compounds was meaningless because of the wide variation in values.

This procedure permitted evaluation of the individual contributions of dispersion, induction, and orientation forces to the apparent internal pressure. The K_s values determined here for nine polar compounds made possible a generalized correlation which eliminates the necessity for having structural constant K_s data which are not available. Dimensional analysis and analogy to Keesom's original unintegrated equation showed that a very simple form would suffice for correlation of polar pressure, namely

$$\omega_i^2 = K_o\left(K_c \frac{\mu_i}{V_{L_i}}\right)^2 \qquad (11)$$

Even though the integrated Keesom equation for the polar part of the internal energy is only an approximation in the case of polar liquids, the values of K_s found for polar compounds were not different enough from the average value for nonpolar compounds to completely discredit the theory. Further, the empirical modifications developed for highly associated compounds allow the polar internal energy to be evaluated for such compounds. This is further borne out by the results of this method. K_o for nonassociated polar compounds has a value equal to 1.0. K_o for associated compounds is always greater than 1.0 and may be evaluated from Figure 2 in which K_o is a function of critical pressure and reciprocal reduced temperature.

Apparent internal pressure is calculated from Equation (9), and the polar pressure contribution is calculated from Equation (11). The nonpolar contribution may then be found from Equation (3).

THE TEST OF VAN ARKEL'S THEORY

Equation (5) was used to calculate the Carlson and Colburn modified van Laar constants. [The saturated liquids volumes at the boiling temperature of the other component of the binary system were calculated by the method of Lyderson, et al. (*11*) which uses a known liquid density for extrapolation to the desired temperature.] These calculated van Laar constants were plotted against the experimentally determined values in Figure 3. The calculated van Laar constants for the polar components lie on a line which curves upward and intersects the 45-deg. line both at the origin and at approximately 0.86. The van Laar constants for the nonpolar compounds did not seem to lie along any curve but were consistently above the curve represented by the data on polar compounds. It was concluded from this that the unmodified van Arkel theory did not form a sound basis for calculation of the van Laar nonideality constants.

EMPIRICAL EXTENSION

Equation (6) indicates that the ratio of the van Laar constants should be the same as the ratio of the molar liquid volumes of the two components in the solution. For polar-nonpolar binaries however this is not the case. Almost without exception the nonpolar component has a larger molal liquid volume and a smaller van Laar constant than the polar component. This causes the ratio of the nonpolar component volume to the polar component volume to be greater than one, while the ratio of the nonpolar component A-value to the polar component A-value is less than one. This observation has been called reversing the asymmetry of the binary system with regard to its activity coefficient composition plot, because the ratio of the limiting logarithms of activity coefficient for the two components will be greater in the case of experimental results. Therefore it was necessary to define an empirical asymmetry constant which would bring theory into agreement with experiment.

$$K_A = \left(\frac{V_{L_i}}{V_{L_j}}\right)\left(\frac{A_{ji}}{A_{ij}}\right)\left(\frac{T_i}{T_j}\right) \qquad (12)$$

The calculated van Laar constant for the nonpolar component was divided by the asymmetry factor to reduce the numerical value of the calculated constant so that it lay on a straight line joining the reduced nonpolar constant and the calculated polar constant. This straight line was parallel to the 45-deg line but was still displaced from the 45-deg. line by the amount of the calculated van Laar constant for the polar component as shown in Figure 3. The asymmetry factor was found to be a function of the absolute magnitude of the difference in the square root of internal pressure as shown in Figure 4. This figure was developed on a purely empirical basis but was found to repro-

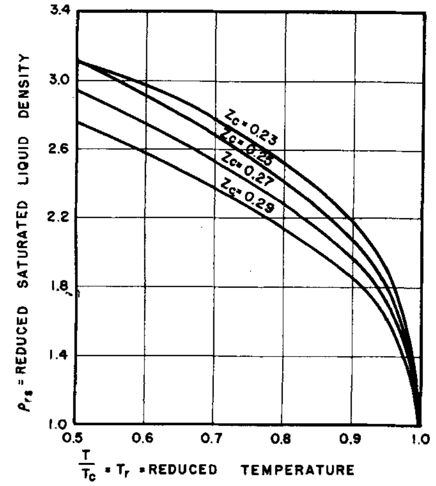

Fig. 6. Reduced saturated liquid density vs. reduced temperature with parameter Z_c as given by Lyderson, et al. (*11*).

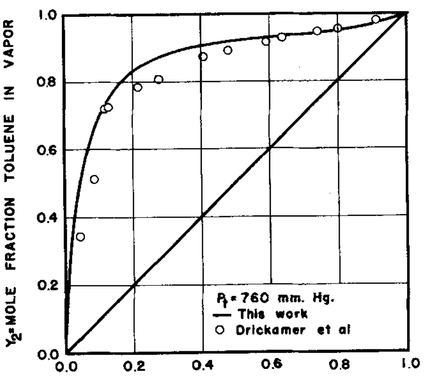

Fig. 7. Binary x-y plot for toluene-phenol at 760 mm. Hg.

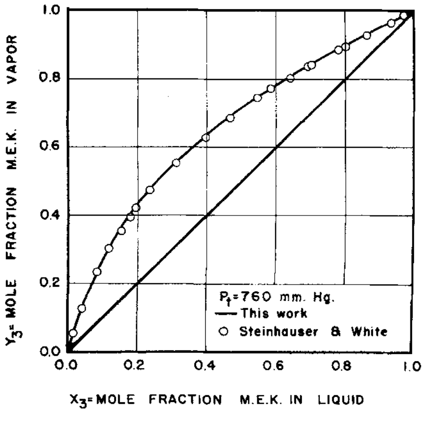

Fig. 8. Binary x-y plot for toluene-methylethylketone at 760 mm. Hg.

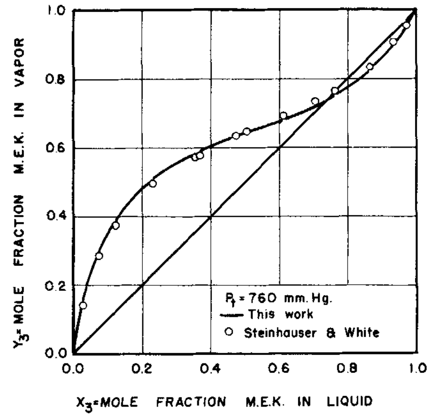

Fig. 9. Binary x-y plot for *n*-heptane-methylethylketone at 760 mm. Hg.

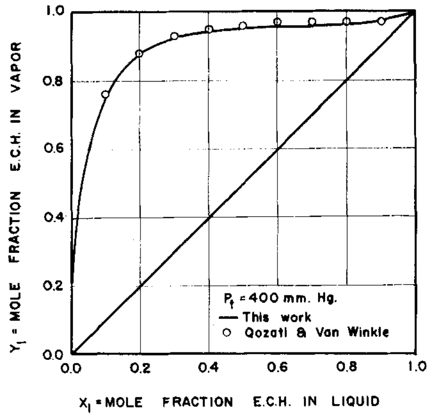

Fig. 10. Binary x-y plot for ethylcyclohexane hexalene glycol at 400 mm. Hg.

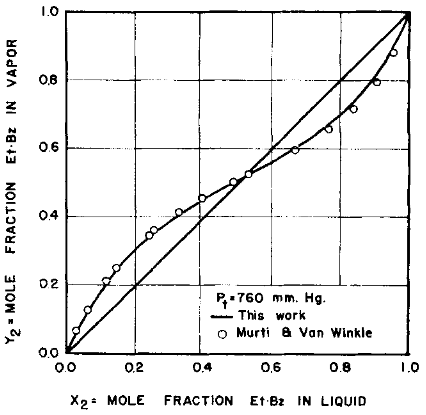

Fig. 11. Binary x-y plot for ethylbenzene cellosolve at 760 mm. Hg.

duce the experimental van Laar constants satisfactorily for the system investigated.

In order to obtain the best possible agreement with the experimental data the deviation of the polar component line on Figure 4 was plotted vs. the calculated value of the van Laar constant for the polar component. This relation, shown in Figure 5, is added algebraically to the calculated values of van Laar constants. This figure is also purely empirical, but the use of Figures 4 and 5 along with the basic theory of van Arkel reproduces the experimental vapor-liquid equilibrium quite well for the systems investigated.

STEP-BY-STEP OUTLINE OF THE METHOD

1. Obtain from the literature or estimate the following properties: critical temperature, critical pressure, critical volume, normal boiling point, saturated liquid volume at reference condition, dipole moment, suitable vapor-pressure data, and representation, for example, Antonine constants. (See references *5, 10, 11, 28.*) (See reference *17* for estimation methods.) (See reference *26* for dipole moments.)

2. Calculate reduced temperature for each component at its own boiling point at the system pressure, at the other component's boiling point at system pressure, and at the temperatures of the available liquid densities.

3. Calculate Riedel's α_c using the normal boiling point, critical pressure, and critical temperature of the component. This procedure is given in Sherwood and Reid (*17*). Use Equation (4-10) and Tables (4-1) and (4-2).

4. Calculate the critical compressibility factor from critical properties obtained in step 1.

5. Calculate F_c by dividing α_c by Z_c.

6. Evaluate the apparent internal pressure.

(*a*) The simplest procedure is to evaluate the reduced temperature at the desired point. Then use Figure 1 to evaluate the reduced apparent internal pressure, with F_c and T_r. Then multiply IP_r by the critical pressure of the component to obtain the apparent internal pressure *IP*.

(*b*) If for any reason you suspect any of the critical properties to be greatly in error, use the following method to evaluate the apparent internal pressure: (1) Use the reduced liquid density chart of Lyderson et al. (Figure 6) to evaluate ρ_{R_1} and ρ_{R_2}. (1 = reference liquid volume temperature. 2 = desired apparent internal pressure temperature.) Calculate $V_2 = \left[\dfrac{\rho_{r_1}}{\rho_{r_2}}\right] V_1$. (2) By means of the Antonine equation calculate the following:

$$P = \exp_{10}\,[A - B/_{C+t}] \quad \text{and}$$

$$\frac{d\ln P}{d\ln T} = \frac{BT}{(C+t)^2}$$

(3) Calculate *IP* by the following equation:

$$IP = P\left[\frac{d\ln P}{d\ln T} - 1\right]\left[\frac{V_g}{V_L} - 1\right]$$

Notes:

(*a*) Be sure vapor pressure is above 100 mm. Hg. abs.

(*b*) Use Z charts in the calculation of V_g is pressure is too high to use ideal gas law.

7. Use Figure 2 to evaluate K_o with T_c and P_c. Then use the following equation to evaluate the polar pressure, ω_i^2:

$$\omega_i^2 = K_o\left[598\,\frac{\mu_i}{V_{L_i}}\right]$$

For the same component of the same temperature calculate δ_i^2 and ω_i^2.

8. Use the method described in 6(*b*) above to evaluate liquid densities of the desired temperatures.

9. Calculate $|(IP_1)^{1/2} - (IP_2)^{1/2}|$ at the boiling temperature of the polar component. Use Figure 4 to evaluate K_A.

10. Calculate A_{ij}'s by the following equations:

$$A_{12} = \frac{V_1[(\delta_1 - \delta_2)^2 + (\omega_1 - \omega_2)^2]}{2.303\,RT_{B_2}} \cdot \frac{1}{K_A}$$

$$A_{21} = \frac{V_2[(\delta_1 - \delta_2)^2 + (\omega_1 - \omega_2)^2]}{2.303\,RT_{B_1}}$$

Where 1 = nonpolar component
2 = polar component
(Note: All quantities in the A_{12} equation are evaluated at T_{B_2} and all quantities in the A_{21} equation are evaluated at T_{B_1}.) . . .

11. Use Figure 5 to obtain the final correction factor which is added algebraically to both calculated A_{ij}'s. (Note: systems composed of an aromatic and a carbonyl compound must use the dotted line on Figure 5).

12. Use A_{ij}'s and vapor-pressure data to calculate vapor-liquid equilibrium data.

DISCUSSION OF RESULTS

The previous section gives the step-by-step method by which vapor-liquid equilibrium data were calculated for twelve polar-nonpolar binary systems (*6, 15, 16, 20, 27*). The results are shown in Figures 7 through 11. Table 1 shows the maximum and average deviations from experimental data.

The average deviation of 1.3 mole % indicates the empirical method outlined here to be very satisfactory for polar-nonpolar systems. The largest deviations encountered were in the binary systems containing phenol (*6*). The investigators encountered immiscibility problems in determining the phenol equilibrium data. This possibly would tend to make the data unreliable. Another possible cause of deviation could be the hydrogen bonding between phenol and toluene.

Table 1 indicates that deviations in terms of relative volatility are relatively five to ten times greater than the deviations in terms of mole percent of calculated vapor composition.

The calculated van Laar binary constants were used to calculate ternary vapor-liquid equilibrium data. Table 1 shows the maximum deviations in terms of relative volatility. Average errors in ternary calculated vapor compositions of between 1 and 5 mole % are estimated for the ternary systems.

The limitations of this method are that it applies to polar-nonpolar binary

TABLE 1. COMPARISON OF PREDICTED WITH EXPERIMENTAL DATA

		Binary				Ternary
No.	System	$\Delta\alpha$ max., %	$\Delta\alpha$ avg., %	Δy max., (mole %)	Δy avg., (mole %)	$\Delta\alpha$ max., %
1	Methylcyclohexane-toluene	6.12	2.9	1.0	0.2	
2	Toluene-phenol	90.3	42.6	15.0	4.0	53.0
3	Methylcyclohexane-phenol	147.2	61.8	11.0	4.4	
4	*n.* octane-ethylbenzene	11.1	3.6	1.0	0.5	
5	Ethylbenzene-cellosolve	12.9	4.7	2.0	1.0	26.0
6	*n.* octane-cellosolve	14.4	7.0	2.7	1.6	
7	*n.* heptane-toluene	12.4	8.0	2.5	0.9	
8	*n.* heptane-methyl-ethyl ketone	11.1	4.7	1.6	1.1	16.9
9	Toluene-methyl-ethylketone	16.6	7.2	1.7	0.5	
10	Ethylcyclohexane-ethylbenzene	6.0	2.9	1.0	0.5	
11	Ethylcyclohexane-hexylene glycol	34.0	16.3	1.5	0.9	12.6
12	Ethylbenzene-hexylene glycol	23.8	12.0	1.8	0.9	
	Averages	30.6%	13.7%	3.3 mole %	1.3 mole %	

and ternary systems, and either to systems which have no hydrogen bonding between unlike components or which have carbonyl-aromatic hydrogen bonding between unlike components.

Several assumptions are made when one uses the van Arkel theory to calculate the vapor-liquid equilibrium data, and these seriously affect the results calculated from equations based on the theory. The most important of these is the assumption that the excess entropy of mixing is zero. Both Barker (*1*) and Murti and Van Winkle (*11*) have indicated that the excess entropy of mixing term $T\Delta S^E$ is far from negligible in both polar-polar and polar-nonpolar systems. Further the term $T\Delta S^E$ is of the same order of magnitude as the term ΔH^E. Therefore by neglecting the excess entropy of mixing about half of the contribution to the excess free energy from which activity coefficients are determined is discarded. The corrections incorporated in the empirical asymmetry constant and its correction factor are probably related to the excess entropy of mixing. Several authors (*7*, *9*) have tried to calculate the excess entropy of mixing as a function of the free volumes of the pure components, but these calculations yield values of excess entropy far smaller than experimental values.

Another assumption is that the integrated Keesom equation, upon which orientation interaction is based, is truly applicable to polar molecules. The integration required to yield the form of the Keesom equation used here depends upon the use of Boltzmann statistics. Boltzmann statistics require that a molecule be free to rotate and have a spherical force field. These limitations are only fulfilled by gases which are weakly polar. Strongly polar liquids do not satisfy these conditions. In addition the average value for the 1-2 dipole interaction might be something other than the geometric mean postulated by van Arkel.

A third assumption which might cause discrepancy between theory and experiment is that molecular shape has no effect on effective volume in solution.

The fourth assumption is that the vapors must be ideal for the apparent and true internal pressures to be equal. This excludes the use of this method at very high pressures, that is above $P_r = 0.35$.

A fifth assumption is that the contribution of induction energy to the internal energy of mixing is negligible. This assumption was completely satisfied in all the systems investigated in this work and is in agreement with the suggestion of van Arkel (*22*).

When one considers all of the assumptions, it is evident that the assumption that the excess entropy of mixing is negligible introduces the most serious error in the theory of solutions where polar molecules are involved.

CONCLUSIONS

Calculations with equations based on the van Arkel theory of solutions indicate that the theory was not adequate for quantitative calculations for polar-nonpolar binary solutions. However empirical extensions presented here make possible quantitative calculations of vapor liquid equilibria for polar-nonpolar binary systems which have no hydrogen bonding between unlike components or which may have hydrogen bonding between carbonyl and aromatic compounds.

Even when the above assumptions were made, the empirical modification of the van Arkel theory gave good reproduction of the experimental vapor-liquid equilibrium data for the binary systems tested in this paper.

The binary van Laar constants were used to calculate ternary vapor-liquid equilibrium data. The ternary data did not agree with experimental data within the same limits of error as the binary data. However the agreement of the ternary calculated data was sufficient to indicate that the method can be used to aid in the selection of solvents for extractive distillation. The greatest error in the van Arkel theory was found to be the neglect of excess entropy of mixing in solutions containing polar molecules.

NOTATION

A = van Laar constant (Carlson-Colburn modification)
A_{ij} = Carlson-Colburn modification of van Laar constant
b_i = leasts squares constants for Equation (9)
C_p = leasts squares constants for Equation (9)
C = ternary van Laar constant
ΔK_v = internal energy of vaporization
F_c = critical parameter for internal pressure correlation α_c/Z_c
ΔG^E = excess free energy of mixing
ΔH^E = excess enthalpy of mixing
IP = apparent internal pressure $(\Delta E_v)/(V_L)$, atm.
k = Boltzmann's constant, erg/molecule °K.
K_A = asymmetry constant (see Figure 5)
K_c = conversion constant for polar pressure equation = 598 when converting from esu. cm./cc./g. mole to atm.$^{1/2}$
K_o = orientation association constant (see Figure 3)
K_s = structural constant = V_{Li}/r_i^3
P = vapor pressure, atm
R = gas law constant, cc. atm./g. mole °K.
ΔS^E = excess entropy of mixing
T = absolute temperature, °K.
T_j = boiling point of component j at pressure of system, °K.
V_g = molar gas volume, cc./g. mole
V_L = molar liquid volume, cc./g. mole
Z_c = critical compressibility factor

Subscripts

i = component i = nonpolar component
j = component j = polar component
r = reduced conditions

Greek Letters

α = molecular polarizability, cc./mole
α_c = $\left(\dfrac{d \ln P}{d \ln T}\right)_c$ = slope of ln P vs.

ln T at the critical point
γ = activity coefficient
δ = square root of nonpolar (dispersion) pressure $= \left(\frac{K}{V_{L_i}}\right) \left(\frac{3}{4} \alpha_i h\nu_i\right)^{1/2}$ = Hildebrand's solubility parameter for nonpolar molecules, atm.$^{1/2}$
μ = dipole moment, esn. cm.
ν = dispersion frequency, sec.$^{-1}$
ϕ_i = effective volume fraction $\frac{X_i V_{L_i}}{\sum\limits_{i=1} X_i V_{L_i}}$
∞ = square root of polar (orientation pressure $= \left(\frac{K}{V_{L_i}}\right) \left(\frac{2}{3} \frac{\mu_i^4}{kT}\right)^{1/2}$ = polar pressure of van Arkel, atm.$^{1/2}$

LITERATURE CITED

1. Barker, J. A., et al., *J. Chem. Phys.*, **19,** 1430 (1951); **20,** 1526 (1952); **21,** 1391 (1953); **22,** 375 (1954).
2. Bromley, E. C., and Dorothy Quiggle, *Ind. Eng. Chem.*, **25,** 1136 (1933).
3. Carlson, H. C., and A. P. Colburn, *ibid.*, **34,** 581 (1942).
4. Cheairs, M. N., and E. C. Makin, Paper presented at Am. Chem. Soc. Regional Meeting at St. Louis, Missouri (Dec. 1-3, 1960).
5. Dreisbach, R. R., *Am. Chem. Soc. Adv. in Chem. Series,* No. 15, (June, 1955); No. 22 (March, 1959).
6. Drickamer, H. G., G. G. Brown, and R. R. White, *Trans. Am. Inst. Chem. Engrs.*, **41,** 555 (1945).
7. Finch, R. N., M.S. thesis, Univ. Texas, Austin, Texas (1961).
8. Glasstone, Samuel, "A Textbook of Physical Chemistry," 2 ed., Van Nostrand, New York (1946).
9. Hildebrand, J. H., and R. L. Scott, "The Solubility of Non-electrolytes," 3 ed., Reinhold, New York (1955).
10. Kobe, K. A., and R. E. Lynn, *Chem. Rev.*, **52,** 121 (1953).
11. Lyderson, A. L., R. A. Greenkorn, and O. A. Hougen, *Rept. No. 4,* Engineering Experiment Station, Univ. Wisconsin, Madison, Wisconsin (1955).
12. Moelwyn-Hughes, E. A., "Physical Chemistry," Pergamon Press, New York (1957).
13. Murti, P. S., and Mathew Van Winkle, *A.I.Ch.E. Journal,* 3, 517 (1957).

13*a*. Perry, J. H., "Chemical Engineer's Handbook," 3 ed., McGraw-Hill, New York (1950).

14. Prausnitz, J. M., and Ralph Anderson, *A.I.Ch.E. Journal,* **1,** 96 (1961).
15. Qozati, Ahmad, and Matthew Van Winkle, *J. Chem. Eng. Data,* **5,** 269 (1960).
16. Quiggle, Dorothy, and M. R. Fenske, *J. Am. Chem. Soc.*, **59,** 1829 (1937).
17. Reid, R. C., and T. K. Sherwood, "The Properties of Gases and Liquids," McGraw-Hill, New York (1958).
18. Riedel, L., *Chem. Eng. Tech.*, **26,** 83 (1954).
19. Robinson, C. S., and E. R. Gilliland, "Elements of Fractional Distillation," 4 ed., pp. 285-289, McGraw-Hill, New York (1950).
20. Steinhauser, H. H., and R. R. White, *Ind. Eng. Chem.*, **41,** 2912 (1949).
21. Union Carbide Chemical Company, "Physical Properties of Synthetic Organic Compounds" (1958).
22. van Arkel, A. E., *Trans. Faraday Soc.*, **42B,** 81 (1946).
23. ———, and S. E. Vles, *Rec. trav. Chim.*, **55,** 407 (1936).
24. van Laar, J. J., Z. *physik. Chem.*, **72,** 723 (1910); **83,** 599 (1913).
25. ———, and R. Z. Lorentz, *anorg. allgem. Chem.*, **146,** 42 (1925).
26. Wesson, L. G., "Tables of Electric Dipole Moments," The Technology Press, Mass. Inst. Technol., Cambridge, Massachusetts (1948).
27. Yang, C. P., and Matthew Van Winkle, *Ind. Eng. Chem.*, **47,** 293 (1935).

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A Theoretical Correlation of Spray-Dryer Performance

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Spray dryers, because of their effective contact between heating medium and particles undergoing drying, are potentially applicable to the widest variety of materials. However their use has been retarded by the lack of reliable engineering procedures for scaling up and analyzing performance. Many studies have been made of the individual factors involved in the spray-drying process (*3, 7, 8*). To facilitate scale up and permit design from basic fundamentals a unifying theory has been needed to tie these factors together.

In this development of an overall correlation of spray-dryer performance the author has calculated the capacity heat transfer or production rate based on the heat transfer rate to the largest spray particles. The production rate, which also is calculated from heat and material balances, is limited by the requirement that the largest particles be dried during their flight from the atomizer to the chamber wall. The time of flight of the largest particles is determined from a consideration of the fluid dynamics of the process. Thus, from a theoretical analysis based on the computation of minimum heat transfer rates (for this case of gas-phase resistance limiting) at capacity conditions (as determined by incipient wall deposition), expressions have been developed which relate overall performance to the dryer geometry, drying temperature, atomizer type, and particle size of the material produced.

With these expressions agreement between predicted and measured heat transfer rates has been obtained for drying of sodium sulfate solutions in 1-, 2-, and 3-ft. diam. dryers and calcium carbonate slurries in the 2-ft. diam. dryer. The obtainable useful rates however are 52% above the minimum rates predicted by these expressions. This agrees with the observation that drops of sodium sulfate solution and calcium carbonate slurries do not require complete drying if they are to be free flowing and are not to stick to the dryer walls. Materials which exhibit less stickiness than sodium sulfate when partially dried have been processed at greater rates than sodium sulfate, whereas materials which exhibit greater stickiness have not.