Vapor Pressures and Interaction Constants of Some Nearly Ideal Solutions

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Total and differential vapor pressures were determined for solutions of isopentane-*n*-pentane, *n*-hexane-*1*-hexene, *n*-pentane-*n*-hexane, and isopentane-*n*-hexane. The nearly ideal solution interaction constants were evaluated for these systems based on the data.

The experimental study of the nonideal behavior of liquid solutions becomes simplified when the experiment is carried out at low-pressure conditions. The departure of the vapor phase from ideal gas behavior is small, and a reliable estimate can be made for this small departure for many systems. As a result, isothermal total vapor-pressure data at a number of compositions suffice for the description of nonideal solution behavior. For this purpose, the data are analyzed in terms of an assumed expression of activity coefficients such as the Wilson equation or one of the Redlich and Kister equations. The adjustable parameters in the equation are determined so as to reproduce the total vapor-pressure data with minimal errors. The procedure has been much used for the study of binary solutions (*9*). Sampling and analysis of the vapor phase are avoided. Analysis of the liquid can also be avoided by careful gravimetric or volumetric preparation of the solution from pure liquids.

The total vapor-pressure method is particularly adapted to the study of nearly ideal solutions. These are made of highly similar components and show small but significant deviations from ideal solution behavior. The deviations are represented by first-order conformal solution equations (*5*). Experimental observations (*10*) showed that the activity coefficients γ in binary nearly ideal solutions follow the simple equation

$$\ln \gamma_1 = Bx_2^2, \quad \ln \gamma_2 = Bx_1^2 \qquad (1)$$

where x denotes the mole fraction in the liquid, and B is a constant. Equation 1 was confirmed by the first-order conformal solution theory which also expresses that

$$B = \frac{(\tilde{U} - \tilde{U}^*)^0}{RT} d_{12} \qquad (2)$$

where $\tilde{U}$ denotes the internal energy per mole. The superscript * denotes the ideal gas state, and 0 refers to the reference fluid. d_{12} is an interaction constant defined with respect to a reference fluid to characterize the 1–2 pairwise interaction (*5*). The internal energy deviation function $(U - U^*)$ has been correlated in a generalized reduced form (*6*). As a result, we need only to know d_{12} to describe the nonideal solution behavior of nearly ideal solutions. The thermodynamics of nearly ideal systems was presented elsewhere (*5*).

Equation 1 shows that the excess quantities of a binary nearly ideal solution are at a maximum at the equimolar composition. The value of the maximum is small; the variation of the excess quantities is extremely small at the neighborhood of the equimolar composition. The most sensitive experimental measurement of the nonideality of nearly ideal solutions should therefore be carried out for nearly equimolar mixtures. We accordingly performed total and differential vapor-pressure measurements for nearly equimolar solutions.

Apparatus and Procedure

We built a static isoteniscope for this work. Figure 1 shows the scheme, which is similar to the apparatus of Davison et al. (*3*). Flask 1 contains about 20 ml of a pure liquid. Flask 3 contains about 20 ml of the solution of interest. The total vapor pressures of the pure liquid in Flask 1 and the solution in Flask 3 are obtained successively from the mercury manometer while the other side of the manometer is evacuated to a pressure below 0.005 mm Hg which is read with a McLeod gage. The difference between the two vapor pressures is also obtained directly from the same manometer by connecting its two sides to the flasks. The mercury levels in the manometers are read to ±0.05 mm with a Fischer Scientific Co. 100-cm range cathetometer.

The solution in Flask 3 is prepared by transferring pure liquids from Flask 2. The stopcock of Flask 2 is of such a construction that a well-defined and reproducible volume of liquid is trapped in it when full. Flask 2 acts like a

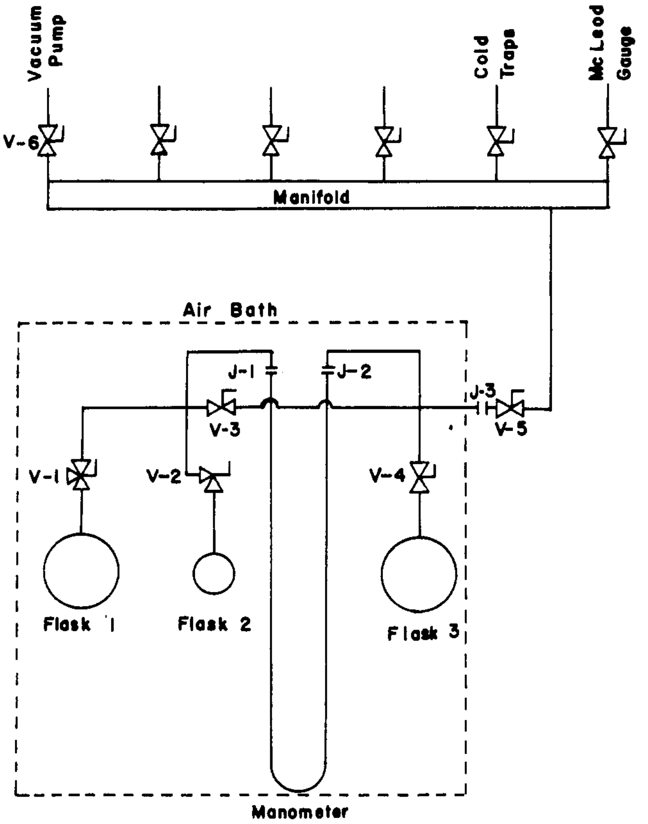

Figure 1. Schematic of vapor-pressure apparatus

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buret. Two flasksful of each pure liquid are transferred from Flask 2 into Flask 3 to prepare the solution for study. Transfer of material in the apparatus is by means of distillation. The rest of the apparatus is closed off, leaving the source connected only to the receiver. Transfer proceeds rapidly when the source is kept at or slightly above room temperature, and the receiver is submerged in liquid nitrogen.

The apparatus was thoroughly tested to be free of leaks before use. The high-vacuum greaseless stopcocks and 0-ring joints that we adopted contributed greatly to our success in achieving leakproof operation. The stopcocks were made by West-Glass Corp., El Monte, Calif. Referring to Figure 1, the catalog numbers are: V1, W-1846; V2, W-1855; V3, V4, and V5, W-1831. The 0-rings were obtained from Delmar Scientific Laboratories, Inc., Maywood, Ill.

An air bath encloses the three flasks, the manometer, the connecting lines, stopcocks, and 0-ring joints. The construction of the air bath was described (7). Temperature control is provided by a Hallikainen Instruments Thermotrol Model 1053 with a Model 1107 resistance thermometer. Temperature control is ±0.01°C. The temperature was measured with a Fischer Scientific Co. precision mercury-in-glass thermometer, total immersion type, with graduations of 0.1°C. It was calibrated against a platinum resistance thermometer with certified calibration by the National Bureau of Standards.

All liquids are thoroughly degassed in Flask 1 before being transferred to other flasks. Degassing is achieved by flashing at room temperature, followed by pumping at high vacuum (0.005 mm Hg or below), while the material is frozen with liquid nitrogen. The procedure is repeated until the vapor pressure no longer changes. The pure liquid-vapor pressures obtained in this work are in good agreement with values adopted by the American Petroleum Institute Research Project 44. An additional description of the apparatus and procedure may be found elsewhere (*4*).

Materials

The pure liquids used in this work were all Phillips Petroleum Co. research-grade products with stated minimum purities as follows: *n*-hexane, 99.99 mol %; *n*-pentane, 99.98 mol %; isopentane, 99.99 mol %; 1-hexene, 99.98 mol %. They were used without additional purification except for degassing as described above.

Data and Analysis

Table I presents data of 10 experimental runs on four binary systems. Several of the runs were duplicates and triplicates that were made in the beginning of the experimental work to check out thoroughly the apparatus and procedure. They are all included in Table I to give a clear indication of the accuracy of the data. Each experimental run includes the vapor pressures of the two pure liquids, the total vapor pressure of their equivolume mixture, and the differences in vapor pressure between the mixture and the two pure liquids. The differential pressures presented in the table are direct manometer readings, not algebraic differences of the three vapor-pressure values.

The data in Table I were analyzed in much the same way as described by Redlich and Kister (*10*). In view of the low pressure of the system, the equilibrium condition is expressed by

$$x_i \gamma_i \theta_i = y_i p \tag{3}$$

where y denotes mole fraction in the vapor; p, the total pressure; and θ is given by

$$\theta_i = p_i^0 \exp\left[\frac{(\tilde{V}_i - B_i)(p - p_i^0)}{RT}\right] \tag{4}$$

p^0 stands for vapor pressure; $\tilde{V}$, liquid molar volume; and B, second virial coefficient. The assumptions made in the derivation of Equation 3 are: The second virial coefficient adequately describes departures of the vapor phase from ideal gas laws; the vapor mixture is an ideal solution; and the pure liquid is incompressible in the pressure range from p^0 to p. From Equation 3 we deduce for a binary solution,

$$p = x_1 \gamma_1 \theta_1 + x_2 \gamma_2 \theta_2 \tag{5}$$

For nearly ideal systems, the activity coefficients are given by Equations 1 and 2. The experimental data in Table I enable the determination of the interaction constant d_{12} by referring to these equations and generalized functions (6). The mole fractions of the equivolume mixtures are calculated by referring to the liquid densities tabulated in the American Petroleum Institute Research Project 44. The values of d_{12} that we have determined for the four binary systems studied in this work are presented in Table II.

Table II. Binary Interaction Constant d_{12} for Several Nearly Ideal Systems

System	d_{12}
Isopentane–*n*-pentane	+0.00018 ± 0.00004
n-Hexane-1-hexene	−0.0092 ± 0.0002
n-Pentane–*n*-hexane	+0.0219 ± 0.0005
Isopentane–*n*-hexane	+0.0235 ± 0.0005

Table I. Experimental Total and Differential Vapor-Pressure Data for Equivolume Mixtures

Run no.	System	T, °C	mm Hg p_1^0	p_2^0	p_{total}^0	$(p_{\text{total}}^0 - p_1^0)$	$(p_{\text{total}}^0 - p_2^0)$
3	*n*-Hexane(1)–1-hexene(2)	60.00 ± 0.05	572.74 ± 0.05	679.57 ± 0.05	641.18 ± 0.05	68.43 ± 0.05	−38.39 ± 0.05
4	*n*-Hexane(1)–1-hexene(2)	60.00 ± 0.05	572.73 ± 0.05	679.59 ± 0.05	641.21 ± 0.05	68.40 ± 0.05	−38.42 ± 0.05
5	*n*-Hexane(1)–1-hexene(2)	60.00 ± 0.05	572.73 ± 0.05	679.61 ± 0.05	641.19 ± 0.05	68.41 ± 0.05	−38.40 ± 0.05
1	*n*-Pentane(1)–isopentane(2)	25.20 ± 0.05	516.30 ± 0.05	692.92 ± 0.05	603.78 ± 0.05	85.25 ± 0.05	−91.37 ± 0.05
2	*n*-Pentane(1)–isopentane(2)	25.20 ± 0.05	516.32 ± 0.05	692.92 ± 0.05	603.78 ± 0.05	85.24 ± 0.05	−91.35 ± 0.05
6	*n*-Pentane(1)–isopentane(2)	25.20 ± 0.05	516.32 ± 0.05	692.91 ± 0.05	603.79 ± 0.05	85.25 ± 0.05	−91.35 ± 0.05
15	*n*-Pentane(1)–*n*-hexane(2)	30.00 ± 0.05	614.80 ± 0.05	187.39 ± 0.05	387.32 ± 0.05	−227.48 ± 0.05	203.55 ± 0.05
16	*n*-Pentane(1)–*n*-hexane(2)	30.00 ± 0.05	614.83 ± 0.05	187.44 ± 0.05	387.25 ± 0.05	−227.48 ± 0.05	203.57 ± 0.05
17	Isopentane(1)–*n*-hexane(2)	25.20 ± 0.05	692.92 ± 0.05	151.18 ± 0.05	407.60 ± 0.05	−285.40 ± 0.05	256.35 ± 0.05
18	Isopentane(1)–*n*-hexane(2)	25.20 ± 0.05	692.92 ± 0.05	151.16 ± 0.05	407.60 ± 0.05	−285.40 ± 0.05	256.33 ± 0.05

Discussion

The system *n*-pentane–isopentane was studied by Redlich and Kister (*10*). Excess total pressures were reported for several mixtures of this system. There was unfortunately no mention of the temperature. The d_{12} value that we previously estimated (*5*) from Redlich and Kister's incomplete data is in excellent agreement with the value derived from this work.

Suryanarayana and Van Winkle (*11*) presented vapor-liquid equilibrium data for the *n*-hexane–1-hexene system at 760 mm Hg. Their data are in substantial agreement with ours. For purposes of comparison, we estimate the equimolal mixture of the system to deviate from the ideal solution vapor pressure by 3.0 ± 1.0% based on their data at 760 mm Hg. The same estimate based on our data at lower pressures gives a corresponding deviation of 2.4%.

Beatty and Calingaert (*2*) reported vapor-pressure data for several other nearly ideal systems. These were cited by Hildebrand and Scott (*8*) in the form of percent deviations of the vapor pressure of equimolal mixtures from their ideal solution values. Thus, three systems close to those reported here were cited, namely: *n*-heptane–2,2,4-trimethyl pentane, 0.05% at 97.2°C, *n*-heptane–*n*-octane, 0.6% at 97.2°C, and *n*-heptane–*n*-hexane, 0.9% at 67.5°C. These deviations appear to be much smaller than the corresponding values for our systems. The original data were reported in 1934, and the purity of the hydrocarbons used appeared poor. For example, pure *n*-heptane was reported (*2*) to have vapor pressures of 731.5 and 734.6 mm Hg at 97.2°C, depending on which binary mixture was being discussed, whereas the currently accepted value (*1*) at the referred temperature is 733.0 mm Hg. Our study indicates the accuracy of these data to be questionable.

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Nomenclature

B = constant in Margules two-suffix expression for activity coefficients at a given temperature
B = second virial coefficient, cc/g-mol
d_{12} = nearly ideal solution constant characterizing binary interaction between components 1 and 2
p = absolute pressure, mm Hg
p^0 = vapor pressure, mm Hg
R = gas constant, 62,360 cc mm Hg/g-mol K
T = temperature, K
$\tilde{U}$ = molar internal energy, cc mm Hg/g-mol
x = mole fraction in the liquid phase
y = mole fraction in the vapor phase

Greek Letters

γ = activity coefficient in the liquid phase
θ = imperfection pressure coefficient

Superscripts

$*$ = ideal gas state
0 = reference substance property

Subscripts

i = component in a mixture

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