Vapor–Liquid Equilibrium Behavior of the *n*-Pentane–Ethanol–Acetone Ternary at 372.7 K

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Isothermal vapor–liquid equilibrium measurements are reported for the *n*-pentane–ethanol–acetone ternary at 372.7 K. These measurements were adequately predicted by using several well-known local composition equations (Wilson, NRTL, and UNIQUAC) to represent the excess Gibbs free energy of the liquid phase. The parameters in these equations were obtained by using data already reported in the literature for the constituent binary systems. A slightly better representation of the data of this study was obtained when the excess Gibbs free energy was modeled by the four-suffix Margules equation with three adjustable ternary constants. The data indicate the presence of a ternary maximum pressure azeotrope. Based on the four-suffix Margules equation, the azeotropic pressure was calculated to be 688.0 kPa at *n*-pentane, ethanol, and acetone mole fractions of 0.729, 0.168, and 0.103, respectively. The pressure of the ternary azeotrope is only slightly higher than the *n*-pentane–ethanol binary azeotrope (685.2 kPa) and the *n*-pentane–acetone binary azeotrope (672.3 kPa) while no azeotrope exists for the ethanol–acetone binary.

Introduction

Vapor–liquid equilibrium behavior of polar–nonpolar systems continues to be of interest to individuals working in the field of distillation. Although the a priori prediction of the vapor–liquid equilibrium behavior for systems of this type is a long-term objective, such a treatment will involve a knowledge of molecular interactions that is not presently available. In the meantime, it is desirable to explore the possibility that the vapor–liquid equilibrium behavior of a multicomponent system can be predicted on the basis of information relating to the constituent binary systems. In this study, the vapor–liquid equilibrium behavior of the *n*-pentane–ethanol–acetone ternary was measured at 372.7 K and the results were used to test the possibility of their prediction from previously published information for the *n*-pentane–ethanol (1), *n*-pentane–acetone (2), and ethanol–acetone (3) binaries at the same temperature.

Experimental Section

The materials, procedure, and apparatus used in this study have been discussed elsewhere (*1–3*). However, a different grade of *n*-pentane was used in the present study than was used previously for the *n*-pentane–ethanol (*1*) and *n*-pentane–acetone (*2*) binaries. The *n*-pentane used in the present study was supplied by the Phillips Petroleum Co. and was pure grade with a stated minimum purity of 99 mol %. With the exception of the degassing procedure, previously described (*1–3*), this reagent was used as such.

The only change in the procedure involved the method of charging the equilibrium cell. Since two charging cells were available, one was filled with pure *n*-pentane while the other contained a prescribed mixture of ethanol and acetone, characterized by the composition parameter

$$C = z_2/(z_2 + z_3) \qquad (1)$$

where z_2 and z_3 are the mole fractions of ethanol and acetone, respectively, in the charging cell. A portion of this mixture was introduced into the equilibrium cell to which *n*-pentane was progressively added until the overall mixture in the equilibrium cell contained approximately 50% *n*-pentane. At this time, the procedure was reversed by emptying the equilibrium cell and recharging it with pure *n*-pentane. The ethanol–acetone mixture was then progressively added to the equilibrium cell to cover the range between 50 and 100% *n*-pentane.

Table I. Vapor–Liquid Equilibrium Measurements for the *n*-Pentane (1)–Ethanol (2)–Acetone (3) Ternary at 372.7 K

	mole fraction					
P, kPa	x_1	x_2	x_3	y_1	y_2	y_3
			$C = 0.200$			
486.8	0.084	0.184	0.732	0.297	0.124	0.579
558.5	0.169	0.168	0.663	0.413	0.097	0.490
618.1	0.291	0.146	0.563	0.524	0.087	0.389
647.1	0.399	0.120	0.481	0.574	0.078	0.348
667.4	0.511	0.097	0.392	0.620	0.078	0.302
679.1	0.642	0.075	0.283	0.668	0.074	0.258
680.5	0.743	0.051	0.206	0.729	0.059	0.212
667.4	0.845	0.031	0.124	0.786	0.051	0.163
637.8	0.929	0.014	0.057	0.881	0.031	0.088
			$C = 0.406$			
447.8	0.054	0.388	0.558	0.262	0.241	0.497
546.1	0.156	0.346	0.498	0.438	0.187	0.375
622.6	0.294	0.285	0.421	0.547	0.159	0.294
652.6	0.403	0.243	0.354	0.585	0.148	0.267
672.2	0.509	0.200	0.291	0.641	0.135	0.224
681.5	0.608	0.160	0.232	0.666	0.133	0.201
686.0	0.707	0.118	0.175	0.721	0.117	0.162
683.3	0.805	0.076	0.119	0.753	0.110	0.137
658.8	0.902	0.038	0.060	0.832	0.081	0.087
			$C = 0.601$			
449.9	0.066	0.571	0.363	0.325	0.330	0.345
551.6	0.171	0.509	0.320	0.484	0.261	0.255
619.5	0.294	0.429	0.277	0.584	0.216	0.200
651.2	0.390	0.370	0.240	0.613	0.211	0.176
671.5	0.499	0.303	0.198	0.654	0.193	0.153
685.0	0.609	0.241	0.150	0.687	0.182	0.131
689.5	0.709	0.180	0.111	0.724	0.167	0.109
685.3	0.802	0.120	0.078	0.766	0.149	0.085
658.4	0.917	0.049	0.034	0.845	0.105	0.050
			$C = 0.806$			
356.8	0.029	0.792	0.179	0.209	0.555	0.236
447.8	0.078	0.751	0.171	0.401	0.413	0.186
592.3	0.227	0.629	0.144	0.593	0.294	0.113
641.6	0.356	0.524	0.120	0.648	0.249	0.103
666.4	0.492	0.422	0.086	0.686	0.232	0.082
677.4	0.572	0.350	0.078	0.706	0.221	0.073
685.3	0.676	0.263	0.061	0.731	0.209	0.060
686.0	0.805	0.159	0.036	0.775	0.181	0.044
661.2	0.925	0.060	0.015	0.852	0.129	0.019

Experimental Results

A total of 36 measurements were made for the *n*-pentane–ethanol–acetone ternary at 372.7 K. In particular, nine measurements were made for each of four values (0.200, 0.406, 0.601, and 0.806) of the composition parameter *C*. The compositions of the vapor and liquid phases, as well as the equi-

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librium pressures, are given in Table I.

Discussion

Treatment of Results. A rigorous treatment of vapor–liquid equilibrium requires that, in addition to temperature and pressure, the fugacity of each component in the mixture be the same in both phases

$$f_i^{\mathrm{v}} = f_i^{\mathrm{l}} \qquad (2)$$

Vapor-phase fugacities were calculated in this study by using the pressure explicit virial equation of state truncated after the second term

$$PV/RT = 1 + B/V \qquad (3)$$

where the second virial coefficient for the mixture is $B = \sum_i \sum_j B_{ij} y_i y_j$. The fugacity of component i in the vapor phase is then given by

$$f_i^{\mathrm{v}} = Py_i \exp[(2\sum_j B_{ij} y_j / V) - \ln (PV/RT)] \qquad (4)$$

The liquid-phase fugacity for component i is given in terms of the activity coefficient γ_i and the standard-state fugacity f_i^0 as

$$f_i^{\mathrm{l}} = \gamma_i x_i f_i^0 \qquad (5)$$

Choosing the standard state of component i to be pure liquid i at the temperature and pressure of the mixture, the standard-state fugacity of component i becomes

$$f_i^0 = P_i^{\mathrm{sat}} \exp[(2B_{ii}/V_i^{\mathrm{v}}) - \ln (P_i^{\mathrm{sat}} V_i^{\mathrm{v}}/RT) + (P - P_i^{\mathrm{sat}}) V_i^{\mathrm{l}}/RT] \qquad (6)$$

where eq 3 was used to integrate up to P_i^{sat}, the vapor pressure of pure component i, and where the molar volume of pure liquid i, V_i^{l}, was assumed constant and equal to the saturated liquid molar volume. In eq 6, V_i^{v} is the saturated vapor molar volume of pure component i at the temperature of the mixture. Using eq 4–6, eq 2 may be expressed for each component in terms of experimentally accessible quantities. If expressions for the composition dependence of the activity coefficients are available, then pressure and vapor-phase composition can be calculated given the temperature and liquid-phase composition.

All of the commonly used means for expressing the composition dependence of the activity coefficients are based on expressions for the molar excess Gibbs free energy of the liquid phase. Expressions for the activity coefficients are determined from the excess molar Gibbs free energy using the rigorous relationship

$$\ln \gamma_i = [\partial(nG^{\mathrm{E}}/RT)/\partial n_i]_{T,P,n_j} \qquad (7)$$

where n is the total number of moles of liquid.

Local Composition Equations. Several of the expressions for G^{E} examined in this study are based on the local composition concept. The first of these is the Wilson equation (*4*)

$$G^{\mathrm{E}}/RT = -\sum_i x_i \ln (\sum_j x_j \Lambda_{ij}) \qquad (8)$$

where $\Lambda_{ii} = 1$. By applying eq 7 to eq 8, we obtain the activity coefficient for component i as

$$\ln \gamma_i = 1 - \ln (\sum_j x_j \Lambda_{ij}) - \sum_k x_k \Lambda_{ki} / (\sum_j x_j \Lambda_{kj}) \qquad (9)$$

For a binary system, the Wilson equation contains two adjustable parameters. No additional parameters, beyond those required for the constituent binary systems, are required for systems containing three or more components.

The NRTL (nonrandom two liquid) equation developed by Renon and Prausnitz (*5*) is

$$G^{\mathrm{E}}/RT = \sum_i x_i (\sum_j \tau_{ji} G_{ji} x_j)/(\sum_k G_{ki} x_k) \qquad (10)$$

where $G_{ji} = \exp(-\alpha_{ji}\tau_{ji})$, $\alpha_{ij} = \alpha_{ji}$ and $\tau_{ii} = 0$. The corresponding expression for the activity coefficient of component i is

$$\ln \gamma_i = (\sum_j \tau_{ji} G_{ji} x_j)/(\sum_k G_{ki} x_k) + \sum_j [x_j G_{ij}/(\sum_k G_{kj} x_k)][\tau_{ij} - (\sum_m x_m \tau_{mj} G_{mj})/(\sum_l G_{lj} x_l)] \qquad (11)$$

For a binary system, the NRTL equation contains three adjustable parameters. However, the number of parameters may be reduced to two, by using values of α_{ij} given by Renon and Prausnitz for characteristic mixtures. Like the Wilson equation, the parameters for a multicomponent mixture are all obtained from data for the constituent binary systems.

The UNIQUAC (universal quasi-chemical) equation of Abrams and Prausnitz (*6*) is

$$G^{\mathrm{E}}/RT = \sum_i x_i \ln (\Phi_i/x_i) + (Z/2)\sum_i q_i x_i \ln (\Theta_i/\Phi_i) - \sum_i q_i x_i \ln (\sum_j \Theta_j \tau_{ji}) \qquad (12)$$

where Φ_i, the average segment fraction, and Θ_i, the average area fraction, are defined by

$$\Phi_i = r_i x_i/(\sum_j r_j x_j) \qquad (13)$$

$$\Theta_i = q_i x_i/(\sum_j q_j x_j) \qquad (14)$$

In eq 12–14, $\tau_{ii} = 1$, $Z = 10$, and r_i and q_i are, respectively, measures of molecular van der Waals surface area and volume. Values of q_i and r_i for each component are found by summing individual group contributions presented by Fredenslund et al. (*7*). The activity coefficient for component i is given by

$$\ln \gamma_i = \ln (\Phi_i/x_i) + (Z/2)q_i \ln (\Theta_i/\Phi_i) + l_i - (\Phi_i/x_i)\sum_j x_j l_j - q_i \ln (\sum_j \Theta_j \tau_{ji}) + q_i - q_i \sum_j \Theta_j \tau_{ij}/(\sum_k \Theta_k \tau_{kj}) \qquad (15)$$

where $l_j = (Z/2)(r_j - q_j) - (r_j - 1)$. For a binary system, the UNIQUAC equation contains two adjustable parameters. Once these parameters for all the constituent binary systems are known, no further information is required in order to make calculations for multicomponent systems.

Four-Suffix Margules Equation. Wohl (*8*, *9*) developed the series representation for the excess Gibbs free energy

$$G^{\mathrm{E}}/(RT\sum_i q_i x_i) = \sum_i \sum_j a_{ij} z_i z_j + \sum_i \sum_j \sum_k a_{ijk} z_i z_j z_k + \ldots \qquad (16)$$

where q_i is a measure of molecular size and where $z_i = q_i x_i/(\sum_j q_j x_j)$. By setting $q_i = 1$ and truncating the series after the four-body term, eq 16 becomes the four-suffix Margules equation. For a ternary system, eq 16 becomes, after rearrangement

$$G^{\mathrm{E}}/RT = (G^{\mathrm{E}}/RT)_{1,2} + (G^{\mathrm{E}}/RT)_{1,3} + (G^{\mathrm{E}}/RT)_{2,3} + (A - C_1^* x_1 - C_2^* x_2 - C_3^* x_3) x_1 x_2 x_3 \qquad (17)$$

where $A = (1/2)(A_{12} + A_{21} + A_{13} + A_{31} + A_{23} + A_{32})$ and where

$$(G^{\mathrm{E}}/RT)_{ij} = (A_{ij} x_j + A_{ji} x_i - C_{ij} x_i x_j) x_i x_j \qquad (18)$$

in which $C_{ij} = C_{ji}$. Equation 18 is the four-suffix Margules equation for a binary system and contains the three adjustable parameters A_{ij}, A_{ji}, and C_{ij}. For a ternary system, the three

Table II. Physical Properties at 372.7 K for *n*-Pentane, Ethanol, and Acetone and Their Second Virial Cross-Coefficients

	n-pentane	ethanol	acetone
P_i^{sat}, kPa	586.9	223.4	366.5
V_i^l, cm^3/mol	134.4	64.6	83.8
B_{ii}, cm^3/mol	-692.8	-757.6	-854.2
r_i	3.8254	2.1055	2.5735
q_i	3.316	1.972	2.336

	cross-coeff, B_{ij}, cm^3/mol
n-pentane + ethanol	-435.8
n-pentane + acetone	-529.0
ethanol + acetone	-656.0

adjustable parameters C_1^*, C_2^*, and C_3^* must be obtained from a regression of ternary data. If we apply eq 7 to eq 17, the activity coefficient for component 1 becomes

$$\begin{aligned}\ln \gamma_1 = {} & x_2[2A_{21}x_1(1 - x_1) + A_{12}x_2(1 - 2x_1) + \\ & C_{12}x_1x_2(3x_1 - 2)] + x_3[2A_{31}x_1(1 - x_1) + \\ & A_{13}x_3(1 - 2x_1) + C_{13}x_1x_3(3x_1 - 2)] + \\ & x_2x_3[3C_{23}x_2x_3 - 2A_{23}x_3 - 2A_{32}x_2] + x_2x_3[A(1 - 2x_1) - \\ & C_1^*x_1 - (1 - 3x_1)(C_1^*x_1 + C_2^*x_2 + C_3^*x_3)] \quad (19)\end{aligned}$$

The expression for $\ln \gamma_2$ is obtained from eq 19 by replacing subscript 1 with 2, 2 with 3, and 3 with 1 while that for $\ln \gamma_3$ is obtained from eq 19 by replacing subscript 1 with 3, 3 with 2, and 2 with 1.

Three special cases of eq 17 were examined in the present study in addition to the complete form. For case 1, the approximation given by Van Ness and Abbott (*10*)

$$G^E/RT = \sum_{\text{all pairs}} (G^E/RT)_{ij} \quad (20)$$

was used. Equation 20 can be reduced to eq 17 by neglecting the terms multiplying $x_1x_2x_3$. For case 2, the parameter A in the terms multiplying $x_1x_2x_3$ was retained, but it was assumed that $C_1^* = C_2^* = C_3^* = 0$. Both cases 1 and 2 require only information relating to the constituent binary systems to make vapor–liquid equilibrium calculations for the ternary system. For case 3, it was assumed that $C_1^* = C_2^* = C_3^*$ while case 4 is represented by eq 17 in its complete form. Both cases 3 and 4 require regression of the ternary data in addition to parameters obtained from data for the constituent binary systems.

Application to the Constituent Binary Systems. Vapor–liquid equilibrium data are available at 372.7 K the for *n*-pentane–ethanol (1), *n*-pentane–acetone (2), and ethanol–acetone (3) binaries. Pure component vapor pressures, saturated liquid volumes, second virial coefficients and UNIQUAC parameters are given for each of the three pure components in Table II. Values for the second virial cross-coefficients are also given in this table. The methods used to calculate the second virial coefficients and saturated liquid volumes have been discussed elsewhere (*1–3*). The vapor pressures given in Table II are averages of those values reported for the binary systems.

The binary data were regressed in a manner similar to that suggested by Barker (*11*) in which only P–x data were used. Optimal values of the parameters in the Wilson, NRTL, UNIQUAC, and four-suffix Margules equations were obtained in this manner and are given in Table III. The NRTL equation was examined in both its two-parameter and three-parameter forms. For the two-parameter model, values of α_{ij} recommended by Renon and Prausnitz were used while values of α_{ij} for the three-parameter model were obtained from the nonlinear regression analysis.

Root mean square deviations in pressure and vapor-phase composition are also given in Table III for each method. For the ethanol–acetone binary all methods yielded the same deviations in pressure and vapor-phase composition. It should be noted that the data for the ethanol–acetone binary were well represented by the three-suffix Margules equation. Thus, C_{ij} in eq 18 was set equal to zero for this system. For the *n*-pentane–acetone binary, the four-suffix Margules equation and the three-parameter NRTL equation yielded the lowest deviations in pressure while the UNIQUAC and two-parameter NRTL equations yielded the highest. The deviations in vapor-phase composition were about the same for all methods. For the *n*-pentane–ethanol binary, the Wilson and three-parameter NRTL equations yielded the lowest deviations in pressure while the UNIQUAC equation produced the highest. With the exception of the UNIQUAC equation, all methods yielded essentially the same deviations in vapor-phase composition.

Table III. Summary of Parameters and Resulting Deviations for the Constituent Binary Systems of the *n*-Pentane (1)–Ethanol (2)–Acetone (3) Ternary at 372.7 K

Wilson

			root mean square	
	Λ_{ij}	Λ_{ji}	Δy_1	ΔP, kPa
12	0.3427	0.1956	0.006	1.0
13	0.4937	0.4772	0.014	2.0
23	0.7700	0.8092	0.008	0.7

NRTL (Two-Parameter)

				root mean square	
	τ_{ij}	τ_{ji}	α_{ij}	Δy_1	ΔP, kPa
12	1.5446	1.1005	0.47	0.006	2.1
13	0.6867	0.6367	0.30	0.015	3.0
23	0.1889	0.2726	0.30	0.008	0.7

NRTL (Three-Parameter)

				root mean square	
	τ_{ij}	τ_{ji}	α_{ij}	Δy_1	ΔP, kPa
12	1.5909	1.1579	0.4974	0.006	1.4
13	0.8490	0.8273	0.7215	0.013	0.6
23	0.2458	0.2651	1.0257	0.008	0.7

UNIQUAC

			root mean square	
	τ_{ij}	τ_{ij}	Δy_1	ΔP, kPa
12	0.2851	1.1527	0.010	7.9
13	0.5302	1.0931	0.015	3.1
23	1.0737	0.7337	0.008	0.7

Four-Suffix Margules

				root mean square	
	A_{ij}	A_{ji}	C_{ij}	Δy_1	ΔP, kPa
12	1.8881	2.1864	0.8399	0.007	2.2
13	1.2814	1.2978	0.4222	0.013	0.6
23	0.4459	0.4408	0.0000	0.008	0.7

Table IV. Comparisons between Experimental Data and Calculations Made Using Local Composition Models for the *n*-Pentane–Ethanol–Acetone Ternary at 372.7 K

	root mean square deviations			
	Δy_1	Δy_2	Δy_3	ΔP, kPa
Wilson	0.007	0.005	0.006	4.9
NRTL (two-parameter)	0.009	0.005	0.007	6.9
NRTL (three-parameter)	0.007	0.006	0.006	3.8
UNIQUAC	0.010	0.006	0.008	8.6

Treatment of the Data for the n-Pentane–Ethanol–Acetone Ternary at 372.7 K. Using the parameters given in Table III, pressure and vapor-phase composition were calculated as a function of liquid composition for the *n*-pentane–ethanol–acetone ternary at 372.7 K. The results of these calculations for the Wilson, two-parameter NRTL, three-parameter NRTL, and UNIQUAC equations were compared with the experimental data to produce the root mean square deviations given in Table IV. These deviations show that all methods are capable of

Table V. Parameter Values and Resulting Root Mean Square Deviations from the Application of the Four-Suffix Margules Equation to the *n*-Pentane-Ethanol-Acetone Ternary at 372.7 K

					root mean square deviations			
case	A	C_1^*	C_2^*	C_3^*	Δy_1	Δy_2	Δy_3	ΔP, kPa
1	0	0	0	0	0.054	0.030	0.037	55.7
2	3.7702	0	0	0	0.008	0.007	0.006	7.3
3	3.7702	0.1862	0.1862	0.1862	0.009	0.006	0.007	6.4
4	3.7702	1.0417	−0.4021	−0.5253	0.007	0.007	0.006	2.6

predicting fairly well the vapor–liquid equilibrium behavior of this ternary system. The ability of each method to predict the behavior of the ternary system appears to be roughly proportional to its ability to model the vapor–liquid equilibrium behavior of the constituent binary systems. However, the fact that the deviations in pressure are, without exception, higher for the ternary system than for the constituent binary systems, indicates that there is some room for improvement in expressing the dependence of the excess Gibbs free energy on composition.

Parameter values and root mean square deviations in pressure and vapor-phase composition for all four cases of the four-suffix Margules equation are given in Table V. Since cases 1 and 2 require only data for the constituent binary systems, the comparison of experimental and calculated values of pressure and vapor-phase composition were made in the same manner described for the local composition models. For cases 3 and 4, all 36 ternary measurements were regressed to determine optimal values for C_i^*. These values for C_i^*, as well as the resulting root mean square deviations in pressure and vapor-phase composition, are given in Table V.

Although all of the parameter values used for cases 1 and 2 were obtained from data for the constituent binary systems, the root mean square deviations are significantly larger for case 1. This may be due to the fact that parameter A includes a number of two-body terms while C_i^* contains only three-body and higher terms. Furthermore, case 2 is consistent with Wohl's expansion while case 1 is not, since for case 1 the influence of two-body terms is neglected in the term multiplying $x_1x_2x_3$ in eq 17, but is retained in the $(G^E/RT)_{ij}$ terms as shown in eq 18.

For this particular ternary system, the approximation for case 3 that $C_1^* = C_2^* = C_3^*$ does not show a large improvement over case 2. Thus, if the ternary data are to be regressed, no advantage is gained by making this assumption. An exception to this point would be if only one or two ternary points were available.

Case 4 shows the smallest root mean square deviation in pressure of all methods examined in this study. This is to be expected since this case makes use of three adjustable ternary parameters. Thus, if one is interested in predicting the vapor–liquid equilibrium behavior of a ternary system of the type examined in this study, the local composition models or case 2 of the four-suffix Margules equation may be used. However, if one is interested in representing a set of ternary data analytically, case 4 of the four-suffix Margules equation provides a useful means of smoothing the data.

***Azeotropic Behavior*.** The fact that several of the measured equilibrium pressures for the *n*-pentane–ethanol–acetone ternary are higher than any pressures measured for the constituent binary systems indicates the presence of a ternary azeotrope. Using case 4 of the four-suffix Margules equation and a flexible polyhedron search, the azeotropic pressure was calculated to be 688.0 kPa at mole fractions of 0.729, 0.168, and 0.103 for *n*-pentane, ethanol, and acetone, respectively. The same approach was applied to the *n*-pentane–ethanol and the *n*-pentane–acetone binaries. For the *n*-pentane–ethanol binary, the azeotropic pressure was calculated to be 685.2 kPa at a *n*-pentane mole fraction of 0.772 while the azeotropic pressure for the *n*-pentane–acetone binary was found to be 672.3 kPa at a *n*-pentane mole fraction of 0.699. No azeotropic behavior was found to exist for the ethanol–acetone binary at 372.7 K.

Glossary

a	parameter in Wohl's expansion (eq 16)
A	parameter in Margules equation (eq 17)
B	second virial coefficient, cm^3/mol
C	composition parameter (eq 1)
C	parameter in Margules equation (eq 17)
f	fugacity, kPa
G	Gibbs free energy, kJ/mol
G	parameter in NRTL equation (eq 10)
l	parameter in UNIQUAC equation (eq 15)
n	number of moles
P	pressure, kPa
q	molecular surface area (eq 12)
q	parameter in Wohl's expansion (eq 16)
r	molecular volume (eq 12)
R	gas constant
T	absolute temperature, K
V	molar volume, cm^3/mol
x	liquid mole fraction
y	vapor mole fraction
z	mole fraction (eq 1)
z	normalized fraction (eq 16)
Z	parameter in UNIQUAC equation (eq 12)

Greek Letters

α	parameter in NRTL equation (eq 10)
γ	activity coefficient
θ	average area fraction (eq 14)
Λ	parameter in Wilson equation (eq 8)
τ	parameter in NRTL equation (eq 10)
τ	parameter in UNIQUAC equation (eq 12)
Φ	average segment fraction (eq 13)

Superscripts

E	excess properties
l	liquid state
sat	saturated state
v	vapor state
0	standard state
*	ternary

Subscripts

i	component i
j	component j
k	component k
l	component l
m	component m
1	*n*-pentane
2	ethanol
3	acetone

Registry No. Acetone, 67-64-1; ethanol, 64-17-5; pentane, 109-66-0.

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Practical Osmotic Coefficients and Excess Gibbs Free Energies of Benzene Solutions of Tri-*n*-octylamine and Tri-*n*-octylammonium Bromide at 298.15 K

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The practical osmotic coefficients of benzene solutions of tri-*n*-octylamine up to 6.0 mol kg^{-1}, and tri-*n*-octylammonium bromide up to 1.6 mol kg^{-1}, were measured by the isopiestic technique at 298.15 K. The relations for the concentration dependence of practical osmotic coefficients, solute activity coefficients, and excess Gibbs free energies are given in analytical forms. The nonideality of the systems investigated is discussed on the basis of the structure of the solutions investigated.

Introduction

In connection with a general study of the association of tri-*n*-alkylammonium salts in nonpolar solvents (e.g., ref 1), Klofutar and Paljk (*2*) measured the practical osmotic coefficients of benzene solutions of tri-*n*-octylammonium bromide (TOAHBr) up to 0.3 mol kg^{-1} by the cryoscopic method. Calorimetric measurements (*2*) indicated that the practical osmotic coefficients of benzene solutions of tri-*n*-octylammonium bromide at room temperature should be quite similar to those at the freezing point of benzene.

The aim of the present investigations was to broaden the concentration range of solutions of tri-*n*-octylammonium bromide in benzene to include concentrations where reversal of the association processes of solute molecules may occur (*1*).

Experimental Section

The solvent, reagent grade benzene from the Baker Chemical Co., was stored over molecular sieves (type 4A, Fisher Scientific Co.). Tri-*n*-octylamine (Aldrich Chemical Co.) was distilled and also stored over molecular sieves. The tri-*n*-octylammonium salt was prepared by thoroughly mixing 200 cm^3 of 1 mol dm^{-3} aqueous hydrobromic acid with 200 cm^3 of hexane containing 13 cm^3 of tri-*n*-octylamine. The hexane layer was dried overnight over anhydrous calcium sulfate and the hexane was removed by evaporation. The resulting salt was then recrystallized four times by cooling from a hot saturated hexane solution to the ice point and filtering. The resulting white needles were dried in the dark in a vacuum line until used.

Table I. Molalities of Isopiestic Solutions

m_{DB}/ mol kg^{-1}	m_{TOA}/ mol kg^{-1}	m_{TOA}/ mol kg^{-1}	m_{TOAHBr}/ mol kg^{-1}
0.241	0.250	0.108	0.408
0.523	0.570	0.252	0.680
1.030	1.179	0.395	0.885
1.216	1.401	0.594	1.109
1.751	1.970	0.781	1.273
2.635	2.798	0.875	1.366
2.851	2.994	1.066	1.502
3.586	3.678	1.205	1.595
4.996	4.898		
6.088	5.849		

The isopiestic equilibrations were performed in the same manner as for aqueous solutions (*3*). It was established that equilibrium was reached when the concentration of identical samples were within 0.1% agreement, with one sample losing solvent and the other gaining solvent to attain equilibrium. Dibenzyl (DB) + benzene solutions were used as reference solutions in the case of benzene solutions of tri-*n*-octylamine. To calculate the practical osmotic coefficients of the reference dibenzyl + benzene system at 298.15 K, the relation for the concentration dependence of the practical osmotic coefficient, obtained from the data given in ref *4*, was used in the form

$$\phi_{DB} = 1 + \sum_{i=1}^{2} A_i m_{DB}^{\,i} \qquad (1)$$

where m is the concentration of solute (mol kg^{-1}), and the regression coefficients A_i, calculated by the method of least squares, amount to $A_1 = -0.039$ and $A_2 = 0.0016$, with a standard error of the estimate $s \cong \pm 0.02$.

The practical osmotic coefficents of benzene solutions of tri-*n*-octylamine and tri-*n*-octylammonium bromide, respectively, were calculated from the molality ratio, $R = m_{ref}/m$, and ϕ_{ref} through the relation

$$\phi = \left(\frac{m_{ref}}{m}\right)\phi_{ref} \qquad (2)$$

In calculations of practical osmotic coefficients of benzene solutions of tri-*n*-octylammonium bromide, the values of the

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