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Prediction of Azeotropic Temperatures and Compositions for Ternary Mixtures

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The azeotropic temperatures and compositions for benzene + 2-methyl-2-propanol and cyclohexane + 2-methyl-2-propanol binary systems and benzene + cyclohexane + 2-propanol and benzene + cyclohexane + 2-methyl-2-propanol ternary systems are determined at seven pressures from 13.5 to 101.5 kPa by an azeotropy apparatus using the rectification method. The ternary azeotropic temperatures and compositions are predicted by the Wilson activity coefficient model with the energy parameters estimated from the azeotropic temperatures and compositions for the corresponding binary systems. The predictions compare satisfactorily with the experimental results and indicate that the Wilson equation can be used for predicting ternary azeotropic points.

Introduction

There is a lot of information available on temperatures and compositions of binary azeotropes at normal pressure. By contrast, fewer multicomponent azeotropes including ternary ones have been studied. Prediction of multicomponent azeotropic temperatures and compositions from readily available binary azeotropic data is of practical importance. Methods and techniques for calculating vapor−liquid equilibrium in general can also be used to predict azeotropic temperatures and compositions for multicomponent mixtures.

A method for predicting ternary azeotropic temperatures and compositions from interaction constants of binary azeotropic mixtures in conjunction with binary azeotropic information was reported by Eduljee and Tiwari (1979) according to a general classification of liquids based on their hydrogen bonding capacities. Some correlation equations for expressing vapor liquid equilibrium as a function of liquid composition were proposed and tested by Tamir (1981).

On the basis of these correlations, equations for predicting azeotropic temperatures and compositions of multicomponent mixtures were derived, and some ternary azeotropes were predicted. On the basis of the topographic feature of the ternary systems, a simple method for predicating ternary azeotropic data was proposed by Kudryavtseva and Toome (1984). It requires information on binary azeotropes and pure components only.

The azeotropic temperatures and compositions for benzene + cyclohexane, benzene + 2-propanol, and cyclohexane + 2-propanol binary systems were studied at pressures from 17 to 101.3 kPa by Storonkin and Morachevskin (1957). The benzene + cyclohexane + 2-propanol ternary system was investigated only at 101.3 kPa by Nagata (1964). No data, however, for the benzene + cyclohexane + 2-methyl-2-propanol are reported.

Experimental Section

Apparatus. The azeotropy apparatus and rectification method described in the previous work (Liao et al., 1991), see Figure 1, is employed for ternary azeotrope determinations. The system pressure is automatically controlled within ±0.1 kPa and determined by a pressure transducer which is calibrated by the vapor pressures of pure water at different temperatures. The azeotropic temperature is measured by a platinum resistance thermometer with a Keithley 195A digital multimeter with an accuracy of ±0.01 K.

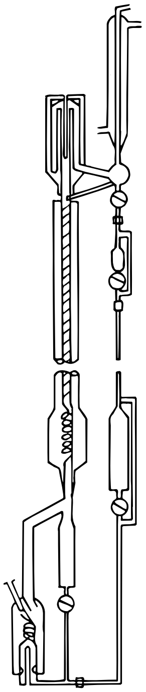

Figure 1. Scheme of the azeotropy apparatus which uses the rectification method.

Chemicals. The benzene, cyclohexane, and 2-propanol are of analytical reagent grade and used as supplied without further purification. The 2-methyl-2-propanol is of chemical pure grade and purified by double crystallization. All the chemicals used in the experimental work are tested by a gas chromatograph, and no other peaks except the major one were detected.

Composition Analysis. The compositions for binary and ternary mixtures are analyzed by a Shimadzu Model GC-7A gas chromatograph equipped with a hydrogen flame detector and a capillary column. The gas chromatograph was calibrated using prepared mixtures. This analytical method was tested using a series of prepared sample

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Table 1. Azeotropic Compositions, Temperatures, and Pressures for Benzene (1) + 2-Methyl-2-propanol (4) and Cyclohexane (2) + 2-Methyl-2-propanol (4)

1 + 4			2 + 4		
P/kPa	T/K	x_1	P/kPa	T/K	x_2
13.59	296.96	0.803	13.46	295.35	0.844
26.43	312.16	0.750	26.51	310.37	0.780
40.23	322.16	0.711	39.75	319.92	0.736
53.29	329.36	0.687	53.60	327.23	0.704
66.69	335.37	0.665	66.62	332.92	0.678
79.76	340.34	0.645	80.16	337.83	0.659
101.51	347.19	0.623	101.40	344.28	0.628

Table 2. Azeotropic Compositions, Temperatures, and Pressures for Benzene (1) + Cyclohexane (2) + 2-Propanol (3) and Benzene + Cyclohexane + 2-Methyl-2-propanol (4)

	1 + 2 + 3			1 + 2 + 4		
P/kPa	T/K	x_1	x_2	T/K	x_1	x_2
13.61	294.14	0.309	0.501	294.91	0.329	0.529
26.64	307.76	0.287	0.470	309.55	0.293	0.506
40.02	317.20	0.275	0.461	319.31	0.257	0.508
53.37	324.72	0.242	0.470	326.88	0.236	0.514
66.63	330.55	0.213	0.465	332.45	0.207	0.515
80.02	335.42	0.200	0.464	337.73	0.165	0.514
101.36	342.19	0.147	0.472	344.25	0.118	0.534
101.33	342.25	0.142	0.474[a]			

[a] Nagata (1964).

mixtures. The average absolute deviation is 0.001 in the mole fraction for binary mixtures and 0.003 mole fraction for ternary mixtures.

Determination of Azeotropes. Initially, a prepared original mixture was distilled for rectification. The light fraction was returned to the rectifying column for about 1 h, and then the light fraction equal to half of the original was collected. For minimum boiling azeotropic systems studied in this work, remnant mixtures in the boiler were replaced by the light fractions for further rectification. In order to ensure that it is just the azeotropic composition for final sampling and measuring, a larger reflux ratio should be maintained and the composition should be analyzed for every circulation during rectification, until both the composition and temperature remain unchanged. The azeotropic temperatures and compositions for benzene (1) + 2-methyl-2-propanol (4), cyclohexane (2) + 2-methyl-2-propanol (4), benzene (1) + cyclohexane (2) + 2-propanol (3), and benzene (1) + cyclohexane (2) + 2-methyl-2-propanol (4) binary and ternary systems were determined at seven pressures from 13.6 to 101.4 kPa by the azeotropy apparatus and are presented in Tables 1 and 2 and in Figures 2–4.

Correlation and Prediction

Correlation of Binary Azeotropes. The variation of azeotropic temperatures with pressure can be correlated by an empirical equation in the form of the Antoine equation

$$\ln(P/\mathrm{kPa}) = A - B/(T(\mathrm{az})/\mathrm{K} + C)$$

where the parameters can be optimized by a linearization algorithm (Chen et al., 1985). The azeotropic compositions can be correlated with temperatures by the linear expression

$$x_1(\mathrm{az}) = a + b(T(\mathrm{az})/\mathrm{K})$$

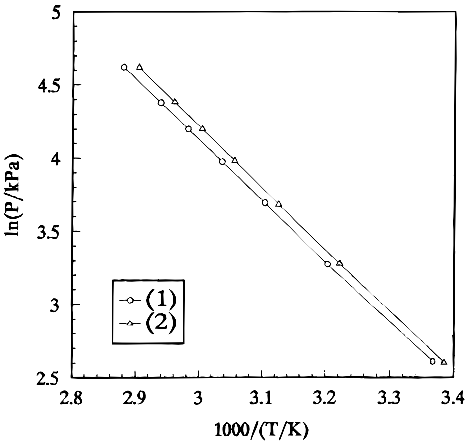

Figure 2. Relationship of azeotropic temperature with pressure for binary systems: (1) benzene + 2-methyl-2-propanol; (2) cyclohexane + 2-methyl-2-propanol.

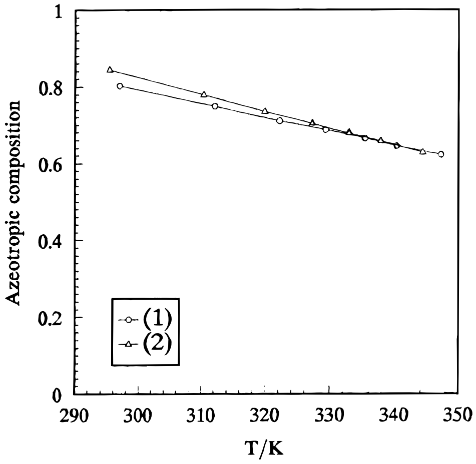

Figure 3. Relationship of azeotropic composition vs temperature for binary systems: (1) benzene + 2-methyl-2-propanol; (2) cyclohexane + 2-methyl-2-propanol.

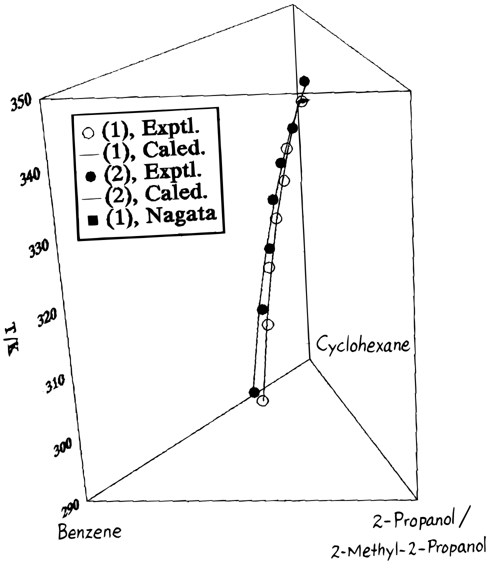

Figure 4. Azeotropic temperature and composition for ternary systems: (1) benzene + cyclohexane + 2-propanol; (2) benzene + cyclohexane + 2-methyl-2-propanol.

In this way, the azeotropic temperatures and compositions for five binary systems are correlated. The optimized parameters and deviations of correlation are presented in Table 3, where r is the linear correlative coefficient.

Prediction of Ternary Azeotropes. The method for predicting ternary azeotropes is to search for a set of equilibrium vapor composition data which exactly equal

Table 3. Optimized Parameters and the Deviations for Binary Systems Containing Benzene (1), Cyclohexane (2), 2-Propanol (3), and 2-Methyl-2-propanol (4)

system	A	B	C	ΔP/%	data source
1 + 2	12.303 06	1988.223	−91.909	0.34	Storonkin et al. (1957)
1 + 3	13.569 11	2364.890	−80.688	0.32	Storonkin et al. (1957)
2 + 3	13.867 24	2474.369	−74.986	0.16	Storonkin et al. (1957)
1 + 4	17.112 21	4517.761	14.488	0.24	this work
2 + 4	17.936 15	4943.692	26.959	0.15	this work

system	a	b	r	Δx_1	data source
1 + 2	0.223 291	0.000 897 7	0.9987	0.0006	Storonkin et al. (1957)
1 + 3	1.858 033	−0.003 639 8	−0.9998	0.0009	Storonkin et al. (1957)
2 + 3	1.870 046	−0.003 703 5	−0.9998	0.0008	Storonkin et al. (1957)
1 + 4	1.873 374	−0.003 604 4	−0.9998	0.0009	this work
2 + 4	2.143 968	−0.004 400 4	−0.9999	0.0008	this work

Table 4. Wilson energy parameters, $\lambda_{ij} - \lambda_{ii}$ and $\lambda_{ji} - \lambda_{jj}$ in J/mol

P/kPa	$\lambda_{12} - \lambda_{11}$	$\lambda_{21} - \lambda_{22}$	$\lambda_{13} - \lambda_{11}$	$\lambda_{31} - \lambda_{33}$	$\lambda_{23} - \lambda_{22}$	$\lambda_{32} - \lambda_{33}$
13.61	621.37	542.57	764.59	5314.92	592.29	8037.15
26.64	797.63	511.68	847.60	5381.06	781.63	8180.64
40.02	812.38	511.36	873.69	5143.70	847.53	7791.64
53.37	795.24	496.86	862.55	4897.68	863.13	7391.29
66.63	773.91	467.14	829.31	4682.85	854.16	7044.43
80.02	757.32	422.44	780.44	4499.45	830.61	6746.61
101.36	750.32	322.39	679.31	4268.99	774.38	6359.14

P/kPa	$\lambda_{12} - \lambda_{11}$	$\lambda_{21} - \lambda_{22}$	$\lambda_{14} - \lambda_{11}$	$\lambda_{41} - \lambda_{44}$	$\lambda_{24} - \lambda_{22}$	$\lambda_{42} - \lambda_{44}$
13.61	621.37	542.57	1073.63	4755.15	−216.76	24238.33
26.64	797.63	511.68	1114.81	3507.88	−29.46	8163.29
40.02	812.38	511.36	992.86	3195.64	52.82	7199.80
53.37	795.24	496.86	848.58	3116.65	100.45	6772.08
66.63	773.91	467.14	712.03	3123.37	136.47	6515.44
80.02	757.32	422.44	586.73	3168.69	169.15	6330.64
101.36	750.32	322.39	412.04	3276.34	220.62	6107.08

the coexisting liquid data. At equilibrium, the fugacities of the vapor and liquid phases must be equal. The deviations of both phases from ideal behavior can be taken into account by

$$Z_i P y_i = \gamma_i p_i^{o} x_i \ (i = 1{-}3) \tag{1}$$

where x and y are mole fractions for the liquid and vapor phases, P is the total pressure, p^{o} is the saturated vapor pressure, γ is the activity coefficient for the liquid phase, and Z is the correction factor for the vapor phase. An alternative form of this equation for calculating vapor composition is

$$y_i = \gamma_i p_i^{o} x_i / Z_i P \tag{2}$$

where Z_i is given by

$$Z_i = \frac{\phi_i}{\phi_i^{o}} \exp\left[\int_{p}^{p_i^{o}} \frac{V_i^{L}}{RT}\, dp\right] \tag{3}$$

The fugacity coefficients ϕ_i can be calculated by using a truncated virial equation of state:

$$Z_i = \exp[(B_i - V_i^{L})(P - p_i^{o})/RT] \tag{4}$$

The second virial coefficients B_i are calculated by the Tsonopoulos (1974) method, where V_i^{L} is the liquid molar volume, calculated from the density, the vapor pressure p_i^{o} is calculated by the Antoine equation with constants taken from the literature (Reid et al., 1977), and the activity coefficients were calculated from the three-component Wilson (1964) equation, as reformulated by Orye and Prausnitz (1965), and are shown below:

$$\ln \gamma_i = 1 - \ln\left[\sum_{j=1}^{3} x_j \Lambda_{ij}\right] - \sum_{k=1}^{3} \frac{x_k \Lambda_{ki}}{\sum_{j=1}^{3} x_j \Lambda_{kj}} \tag{5}$$

$$\Lambda_{ij} = \frac{V_j^{L}}{V_i^{L}} \exp\left[-\frac{\lambda_{ij} - \lambda_{ii}}{\mathrm{RT}}\right] \tag{6}$$

Here $\lambda_{ij} - \lambda_{ii}$ and $\lambda_{ji} - \lambda_{jj}$ are the Wilson paired energy parameters, which are considered temperature indenpendent.

An attempt has been made to predict multicomponent azeotropic points including ternary ones from the corresponding binary azeotropic temperatures and compositions as well as the properties of the pure components by means of the Wilson equation as follows: at the azeotropic point,

Table 5. Prediction of Ternary Azeotropic Temperatures and Compositions

	Predictions				Deviations			
P/kPa	T/K	x_1	x_2	x_3	ΔT	Δx_1	Δx_2	Δx_3
				Benzene (1) + Cyclohexane (2) + 2-Propanol (3)				
13.61	294.08	0.305	0.505	0.191	−0.06	−0.004	0.003	0.001
26.64	307.94	0.288	0.477	0.236	0.18	0.001	0.007	−0.007
40.02	317.37	0.266	0.465	0.269	0.17	−0.009	0.004	0.005
53.37	324.56	0.244	0.460	0.296	−0.16	0.002	−0.010	0.008
66.63	330.42	0.221	0.460	0.319	−0.13	0.008	−0.005	−0.003
80.02	335.48	0.197	0.463	0.340	0.06	−0.003	−0.001	0.005
101.36	342.30	0.156	0.473	0.371	0.11	0.009	0.001	−0.010
				Benzene (1) + Cyclohexane (2) + 2-Methyl-2-propanol (4)				
13.61	294.86	0.333	0.524	0.143	−0.05	0.004	−0.006	0.001
26.64	309.64	0.301	0.507	0.192	0.09	0.008	0.001	−0.009
40.02	319.42	0.268	0.503	0.229	0.11	0.010	−0.004	−0.006
53.37	326.73	0.234	0.505	0.260	−0.15	−0.001	−0.009	0.010
66.63	332.59	0.201	0.511	0.288	0.14	−0.005	−0.003	0.009
80.02	337.56	0.167	0.521	0.313	−0.17	0.001	0.006	−0.008
101.36	344.17	0.109	0.542	0.350	−0.08	−0.010	0.008	0.002

the vapor composition equals that of the liquid, and hence the vapor liquid equilibrium relationship becomes

$$\gamma_i = Z_i P / P_i^{\circ} \tag{7}$$

A pair of activity coefficients can be calculated more exactly from the azeotropic temperatures and pressures using this equation than from a measurement of equilibrium compositions. The activity coefficients from this equation and azeotropic compositions were then substituted into the two-parameter Wilson equation, and a pair of Wilson energy parameters were obtained. In this calculation, the azeotropic temperatures and compositions of the corresponding binary systems were taken from the above equations of correlation. Thus, three pairs of Wilson energy parameters were obtained for calculating the activity coefficients of the ternary systems, which are tabulated in Table 4. To calculate the azeotropic temperature and compositions at a given total pressure, for example, at the experimental pressure, a dual iterative technique was employed. Initially, an arbitrary liquid composition, for example, 0.3333, 0.3333, 0.3334, and an arbitrary temperature were assumed. Then, three activity coefficients were calculated from the three-component Wilson equation. The equilibrium vapor composition was determined via eq 2 by changing the temperature until the summation of the mole fractions for the vapor phase became unity. This temperature is the vapor–liquid equilibrium temperature for the predetermined liquid composition at the given total pressure. If the calculated equilibrium vapor composition is not equal to the liquid composition, which is usually the case at the begining of the iteration, then the liquid composition is replaced by the calculated vapor composition and the previous steps are repeated. When and if this condition is satisfied, the ternary azeotropic point is determined. In this way, the ternary azeotropic temperatures and compositions for benzene + cyclohexane + 2-propanol and benzene + cyclohexane + 2-methyl-2-propanol systems were predicted and compared with the experimental results. The calculated temperatures and compositions are presented in Table 5 and in Figure 4 by solid lines.

Results and Discussion

The experimental work demonstrates that benzene + 2-methyl-2-propanol, cyclohexane + 2-methyl-2-propanol, benzene + cyclohexane + 2-propanol, and benzene + cyclohexane + 2-methyl-2-propanol exhibit minimum boiling azeotropes at subatmospheric pressures. The azeotropic temperatures and compositions are determined at seven pressures from 13.5 to 101.5 kPa for these systems. The relationship between binary azeotropic temperatures and compositions with pressure is studied and correlated by empirical equations. The ternary azeotropes are predicted by the Wilson activity coefficient model from the azeotropic temperatures and compositions for the corresponding binary systems. The calculations satisfactorily agree with the experimental results. It shows that the Wilson equation can be used for predicting ternary azeotropes from the binary azeotropes.

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