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Vapor−Liquid Equilibria of Binary Mixtures Containing Nitroethane with Five Alkyl Esters at 101.3 kPa

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Vapor−liquid equilibria (VLE) were measured at 101.3 kPa, in a range of temperatures from 350.28 to 387.00 K, for five binary mixtures formed by nitroethane with ethyl acetate, propyl acetate, isopropyl acetate, methyl propionate, and ethyl propionate. Calculations of nonideality of the vapor phase were made with the Soave−Redlich−Kwong equation of state. The thermodynamic consistency of the data was tested via Herington analysis. The experimental VLE data were reduced, and binary parameters for four liquid models, such as van Laar, Wilson, NRTL, and UNIQUAC, were fitted. A comparison of model performances was made by using the criterion of average absolute deviations in boiling point and in vapor-phase composition.

Introduction

In this article we present isobaric vapor−liquid equilibria (VLE) data for five binary mixtures with nitroethane as the common component. The other components are ethyl acetate, propyl acetate, isopropyl acetate, methyl propionate, and ethyl propionate. This is part of our research program whose purpose is to contribute to the development of the database for the thermodynamic properties of mixtures of nitroalkanes with various organic solvents. The common nitroalkanes such as nitromethane and nitroethane are high-polarity and moderate boiling point solvents used in a variety of engineering applications. To the best of our knowledge, we are not aware of any extensive mixing property study containing these solvents.

Experimental Section

Materials. Nitroethane, ethyl acetate, propyl acetate, isopropyl acetate, methyl propionate, and ethyl propionate were obtained from different suppliers. All components were dried over molecular sieves (Aldrich, 0.3 nm). Nitroethane and isopropyl acetate were distilled through a glass column (23-mm i.d. and 470-mm length, Teflon mesh packing) under nitrogen. The other components were used without further purification. The purity of all chemicals was checked by gas chromatography (GC) and Karl Fischer titration. In all cases chemicals with a purity greater than 99.5 mass % were used for the experimental investigations. The pure component properties were measured in this work, and comparisons with the published values are shown in Table 1. Densities, ρ, of pure compounds were measured at (298.15 ± 0.01) K using the Anton Paar DMA 58 densimeter with an accuracy of $\pm 1 \times 10^{-2}$ kg/m^3. Refractive indices, n_D, of pure chemicals were measured at (298.15 ± 0.1) K by an Abbe refractometer, Atago RX-5000, with an accuracy of ±0.000 01 unit.

Apparatus and Procedure. The apparatus used was an all-glass equilibrium still (NGW/Germany) with a provision for both vapor and liquid recirculation as described by Hunsmann (1967). The still has a total capacity of about 100 cm^3. The steady conditions were indicated by the constant boiling temperatures of the liquid and vapor phases within the equilibrium cell, and their difference was within 0.02 K. The system was allowed to maintain this equilibrium state for about 30 min before samples were taken. The equilibrium temperature was measured by a calibrated Pt-100 resistance thermometer with an accuracy of ±0.01 K. The pressure was maintained at 101.3 kPa through a manostat pressure control. The accuracy of pressure control was within ±0.1 kPa.

Compositions of sampled liquid and condensed vapor phases were analyzed with a Perkin-Elmer Autosystem gas chromatograph, after calibration with gravimetrically prepared standard solutions. A flame ionization detector was used along with a 60 m × 0.53 mm capillary column packed by Stabilwax. The GC response peaks were integrated by using a Perkin-Elmer 1020 integrator. At least three analyses were made of each liquid and each vapor composition. With these repeated procedures, the accuracy of equilibrium composition measurements was within ±0.001 mole fraction.

Results and Discussion

VLE were measured at 101.3 kPa for five binary mixtures containing nitroethane with ethyl acetate, propyl acetate, isopropyl acetate, methyl propionate, and ethyl propionate. The results are presented in Tables 2−6, respectively. The activity coefficient γ of pure liquid i in a nonideal mixture at temperature T and pressure P was calculated from

$$\phi_i P y_i = \gamma_i P_i^\circ x_i \phi_i^{\mathrm{s}} \exp[v_i^{\mathrm{L}}(P - P_i^\circ)/RT] \qquad (1)$$

where x and y are the liquid and vapor mole fractions in equilibrium, ϕ is the vapor-phase fugacity coefficient, P° is the vapor pressure of the pure component, v^{L} is the liquid molar volume, and superscript s stands for saturation. The vapor-phase fugacity coefficients were calculated from the Soave−Redlich−Kwong (SRK) equation of state (Soave, 1972), where the binary interaction parameter, k_{ij}, was set to be 0. The required pure component data such as vapor pressures, liquid molar volumes, critical properties, and UNIQUAC parameters were taken directly from CHEM-

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Table 1. Densities, Refractive Indices, and Normal Boiling Points of Chemicals Used

	ρ(298.15K)/(kg·m^{-3})		n_D(298.15K)		T_b(101.3 kPa)/K	
compd	this work	lit.	this work	lit.	this work	lit.
nitroethane	1044.51	1044.64[a] 1043.8[b]	1.38987	1.38973[a]	387.00	387.22[a] 387.12[b]
ethyl acetate	894.07	894.55[a]	1.36992	1.36978[a]	350.28	350.261[a]
propyl acetate	882.03	883.03[a]	1.38166	1.3828[a]	374.69	374.686[a]
isopropyl acetate	866.80	870.2[a]	1.37486	1.3750[a]	361.75	361.751[a]
methyl propionate	908.95	909.00[c]	1.37444	1.3742[c]	352.71	352.60[c]
ethyl propionate	883.92	884.0[a]	1.38139	1.3814[a]	372.23	372.25[a]

[a] Riddick et al., 1986. [b] Yoshikawa et al., 1994. [c] TRC, 1996.

Table 2. Vapor−Liquid Equilibrium Data for the Ethyl Acetate (1) + Nitroethane (2) System at 101.3 kPa

T/K	x_1	y_1	γ_1	γ_2
387.00	0.000	0.000		1.000
384.45	0.046	0.121	1.011	0.988
381.39	0.092	0.227	1.024	1.000
379.15	0.136	0.314	1.014	0.998
376.52	0.186	0.403	1.018	1.000
373.68	0.241	0.486	1.022	1.009
371.57	0.290	0.549	1.015	1.013
369.38	0.341	0.603	1.007	1.031
367.56	0.383	0.646	1.010	1.042
365.76	0.430	0.695	1.018	1.032
363.97	0.485	0.739	1.010	1.038
362.33	0.539	0.779	1.004	1.038
360.94	0.583	0.807	1.002	1.051
359.40	0.629	0.833	1.003	1.078
358.19	0.688	0.866	0.988	1.074
356.76	0.742	0.894	0.988	1.080
355.48	0.795	0.920	0.986	1.074
354.28	0.846	0.943	0.986	1.063
352.95	0.899	0.965	0.991	1.048
351.74	0.950	0.983	0.992	1.074
350.28	1.000	1.000	1.000	

Table 3. Vapor−Liquid Equilibrium Data for the Propyl Acetate (1) + Nitroethane (2) System at 101.3 kPa

T/K	x_1	y_1	γ_1	γ_2
387.00	0.000	0.000		1.000
385.68	0.052	0.088	1.237	0.995
384.83	0.099	0.153	1.156	0.997
383.64	0.148	0.220	1.149	1.005
382.71	0.198	0.280	1.122	1.013
382.10	0.247	0.328	1.071	1.026
381.28	0.299	0.384	1.060	1.035
380.44	0.349	0.437	1.058	1.045
379.65	0.398	0.490	1.064	1.049
379.03	0.445	0.534	1.055	1.059
378.54	0.497	0.577	1.035	1.077
378.09	0.550	0.614	1.008	1.114
377.56	0.597	0.658	1.011	1.120
376.96	0.644	0.704	1.020	1.118
376.50	0.699	0.751	1.016	1.129
376.15	0.749	0.792	1.010	1.143
375.81	0.799	0.833	1.006	1.158
375.47	0.851	0.871	0.997	1.220
375.20	0.899	0.916	1.001	1.182
374.89	0.951	0.959	0.999	1.201
374.69	1.000	1.000	1.000	

Table 4. Vapor−Liquid Equilibrium Data for the Isopropyl Acetate (1) + Nitroethane (2) System at 101.3 kPa

T/K	x_1	y_1	γ_1	γ_2
387.00	0.000	0.000		1.000
384.81	0.048	0.106	1.142	0.987
383.13	0.102	0.197	1.051	0.997
381.07	0.158	0.293	1.066	0.996
378.96	0.217	0.376	1.054	1.008
377.64	0.269	0.436	1.022	1.016
375.85	0.322	0.502	1.032	1.022
374.38	0.377	0.562	1.028	1.025
373.20	0.417	0.603	1.031	1.030
371.88	0.465	0.650	1.034	1.033
370.72	0.514	0.682	1.015	1.072
369.73	0.568	0.724	1.003	1.081
368.62	0.603	0.753	1.015	1.092
367.73	0.654	0.786	1.003	1.117
366.73	0.703	0.821	1.003	1.125
365.84	0.755	0.857	1.001	1.123
364.93	0.797	0.882	1.003	1.153
364.17	0.848	0.915	1.000	1.138
363.35	0.898	0.944	0.999	1.148
362.58	0.950	0.974	0.997	1.117
361.75	1.000	1.000	1.000	

Table 5. Vapor−Liquid Equilibrium Data for the Methyl Propionate (1) + Nitroethane (2) System at 101.3 kPa

T/K	x_1	y_1	γ_1	γ_2
387.00	0.000	0.000		1.000
384.67	0.046	0.113	1.003	0.990
381.98	0.094	0.223	1.036	0.989
379.07	0.146	0.326	1.050	0.994
376.70	0.201	0.410	1.020	1.001
374.30	0.248	0.483	1.038	1.005
372.00	0.298	0.541	1.029	1.028
370.21	0.350	0.594	1.010	1.040
368.37	0.398	0.644	1.014	1.046
367.13	0.449	0.689	0.995	1.040
365.14	0.499	0.733	1.008	1.049
363.80	0.542	0.762	1.003	1.070
362.33	0.594	0.805	1.009	1.040
360.93	0.645	0.831	1.000	1.082
359.59	0.694	0.858	0.998	1.105
358.28	0.749	0.889	0.997	1.102
357.27	0.798	0.914	0.992	1.099
356.17	0.847	0.937	0.990	1.106
355.15	0.896	0.960	0.990	1.071
353.40	0.974	0.991	0.993	1.027
352.71	1.000	1.000	1.000	

CAD Data Bank (CHEMCAD Software, 1998). The calculated activity coefficients for the binary systems are also presented in Tables 2−6.

All five binary systems passed the Redlich−Kister thermodynamic consistency test using the Herington analysis (van Winkle, 1967). According to the Herington method, the experimental data are thermodynamically consistent if $D - J$ is less than 10. The Herington's $D - J$ for the Redlich−Kister test was found to be 8.53, 4.28, 0.090, 1.34, and 4.88 for the binary systems of nitroethane with ethyl acetate, propyl acetate, isopropyl acetate, methyl propionate, and ethyl propionate, respectively. The experimental VLE data of the five binary systems were then used to obtain the binary parameters of various activity coefficient models. The van Laar, Wilson, NRTL, and UNIQUAC models were employed in our regressions. The expressions of the activity coefficient by these models were listed in the literature (Prausnitz et al., 1986). Estimation of energy parameters of all the models studied was based on minimization of the objective function F in terms of predicted and experimental γ values. The function F for a

Table 6. Vapor−Liquid Equilibrium Data for the Ethyl Propionate (1) + Nitroethane (2) System at 101.3 kPa

T/K	x_1	y_1	γ_1	γ_2
387.00	0.000	0.000		1.000
386.00	0.050	0.087	1.183	0.984
384.64	0.099	0.161	1.146	0.993
383.43	0.149	0.233	1.139	0.996
382.49	0.196	0.290	1.105	1.003
381.33	0.247	0.350	1.093	1.016
380.33	0.294	0.400	1.079	1.031
379.55	0.343	0.453	1.070	1.034
378.78	0.390	0.494	1.049	1.055
377.97	0.442	0.543	1.041	1.068
377.31	0.491	0.584	1.026	1.087
376.60	0.539	0.622	1.016	1.115
376.03	0.588	0.668	1.017	1.116
375.48	0.637	0.714	1.019	1.110
375.11	0.690	0.750	0.999	1.149
374.63	0.738	0.792	1.000	1.148
374.14	0.793	0.834	0.994	1.178
373.63	0.848	0.878	0.993	1.198
373.25	0.897	0.918	0.993	1.203
372.87	0.948	0.964	0.997	1.059
372.23	1.000	1.000	1.000	

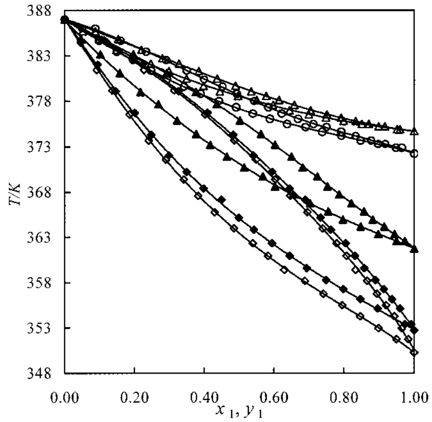

Figure 1. $T-x-y$ diagram for alkyl alkanoates (1) + nitroethane (2) at 101.3 kPa: (△), *n*-propyl acetate; (○) ethyl propionate; (▲) isopropyl acetate; (◆) methyl propionate; (◇) ethyl acetate.

binary system can be stated as

$$F = \sum_{k=1}^{N} \sum_{i=1}^{2} \left[\left(\frac{\gamma_i^{\mathrm{e}} - \gamma_i^{\mathrm{c}}}{\gamma_i^{\mathrm{e}}} \right)^2 \right]_k \qquad (2)$$

where N is the number of data points and the superscripts "*e*" and "*c*" indicate experimental and calculated values, respectively. The fitted parameters for van Laar, Wilson, NRTL, and UNIQUAC, together with the mean values of the absolute deviations in boiling point, ΔT, and in vapor-phase mole fraction, Δy, are shown in Table 7. As can be seen, the deviations of the regressions are reasonably small, and it indicates that all activity coefficient models are adequate to represent the binary experimental data. The experimental $T-x-y$ data for the five systems at 101.3 kPa are reproduced in Figure 1. No azeotropes were found for any of the five systems, and all the liquid-phase activity coefficients are very close to unity; therefore, the ideal mixtures were essentially formed for these systems.

Conclusion

Experimental VLE data on five binary systems formed by nitroethane with ethyl acetate, propyl acetate, isopropyl acetate, methyl propionate, and ethyl propionate at 101.3 kPa have been presented. All five systems passed the Redlich−Kister thermodynamic consistency test using Herington analysis with $D - J < 10$. No azeotropes were found for any of the five systems. Analysis of experimental data for the five binary systems using the van Laar, Wilson, NRTL, and UNIQUAC models shows that all four models are generally satisfactory for all five binary mixtures.

Table 7. Correlation Parameters and the Absolute Average Deviations in Boiling Points and Vapor-Phase Mole Fractions for the Binary Systems[a]

	A_{12}	A_{21}	α_{12}	ΔT/K	Δy_1
	Ethyl Acetate (1) + Nitroethane (2)				
van Laar	0.0668	0.0474		0.23	0.0042
Wilson	−297.55	372.42		0.23	0.0046
NRTL	−7.9492	26.658	0.2874	0.21	0.0041
UNIQUAC	39.756	−26.057		0.23	0.0042
	Propyl Acetate (1) + Nitroethane (2)				
van Laar	0.2671	0.1638		0.18	0.0044
Wilson	46.253	72.526		0.17	0.0042
NRTL	−140.13	245.59	0.2787	0.14	0.0049
UNIQUAC	26.746	11.331		0.17	0.0044
	Isopropyl Acetate (1) + Nitroethane (2)				
van Laar	0.1687	0.1096		0.23	0.0051
Wilson	−11.676	86.608		0.21	0.0049
NRTL	42.859	10.346	0.2904	0.22	0.0062
UNIQUAC	98.007	−61.520		0.18	0.0056
	Methyl Propionate (1) + Nitroethane (2)				
van Laar	0.0872	0.0487		0.22	0.0045
Wilson	58.349	−5.6321		0.22	0.0044
NRTL	−148.79	198.88	0.3278	0.22	0.0046
UNIQUAC	−39.679	55.722		0.22	0.0045
	Ethyl Propionate (1) + Nitroethane (2)				
van Laar	0.2150	0.1262		0.26	0.0050
Wilson	101.24	27.299		0.28	0.0046
NRTL	−218.32	367.65	0.3616	0.29	0.0041
UNIQUAC	−57.796	103.47		0.25	0.0041

[a] The binary adjustable parameters for various models are as follows: Wilson, $A_{12} = (\lambda_{12} - \lambda_{11})/R$, $A_{21} = (\lambda_{21} - \lambda_{22})/R$; NRTL, $A_{12} = (g_{12} - g_{22})/R$, $A_{21} = (g_{21} - g_{11})/R$; UNIQUAC, $A_{12} = (U_{12} - U_{22})/R$, $A_{22} = (U_{21} - U_{11})/R$.

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