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Vapor−Liquid Equilibria in Ethanol + (Butyl Methyl Ether or Dipropyl Ether) Systems at 308.15, 323.15, and 338.15 K

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Isothermal vapor−liquid equilibria measured by an ebulliometric method for ethanol + butyl methyl ether and + dipropyl ether at (308.15, 323.15, and 338.15) K are presented. The ability of the modified UNIFAC, DISQUAC, Nitta-Chao, and modified ERAS models to predict these data has been tested.

Introduction

Thermodynamic properties of mixtures containing hydrocarbons, ethers, and alcohols have attracted a great deal of attention because of an application in gasoline production. Numerous experimental data of mixtures closely resembling industrial blends were published. It seems, however, that still we are far from a quantitative understanding of all the phenomena occurring in these systems. We believe that a proper examination should start from the simplest systems built up from the same functional groups, that is, *n*-alkane + *n*-alcohol + unbranched monoether, although branched ethers represent the main component of gasoline-blending agents. The suggestion to study systems containing unbranched rather than branched ethers stems from the fact that the main interactions, particularly those of strong hydrogen bonding, are practically the same for both kinds of systems. However, up to now, the systems with unbranched ethers have not been described in a satisfactory way, since their properties result from a combination of at least two important effects—the association phenomenon and the packing effect due to branching. As long as one among them is not described separately, the models applied for the branched ethers may be seriously questioned. This work is a continuation of a study in which associational interactions between an alcohol and an ether are being separated and described (Hofman and Casanova, 1997).

Vapor−liquid equilibrium data for ethanol + an unbranched monoether are not numerous. There exist the $p-x-T$ data of Lourder et al. (1924) for ethanol + diethyl ether at eleven temperatures from 273 to 323 K. The only later data are those of Ernst (1975) for ethanol + *n*-propanol at 333.15 K.

Experimental Section

Dipropyl ether (stated purity ≥ 99.5%) and ethanol (99.9%) were obtained from Fluka. Purities were confirmed by gas chromatographic analysis, which gave for the above compounds 99.9% and 99.95%. The content of H_2O in ethanol was found to be <0.01% by the Fischer method. Butyl methyl ether (Fluka, >99%) was twice fractionally distilled using the 10-plates Oldershaw distilling column (Aldrich). The densities and saturated vapor pressures of the components agree well with literature values (Table 1).

The vapor−liquid equilibria were determined by an ebulliometric method (Domańska *et al*., 1996), in which the compositions of both the liquid and the vapor phase mole fractions were analyzed. The overall pressure was controlled in a manner to achieve an assumed system temperature. It was measured using a mercury manometer in which mercury levels were determined with a kathetometer. In an equilibrium state, pressure was constant within ±0.04 kPa and temperature within ±0.02 K. The latter quantity was measured using a calibrated platinum resistance thermometer (Frontec S1223).

The compositions of the liquid and vapor phases were determined by density measurements using an Anton Paar DMA 02C vibrating tube densimeter described in a paper by Witek et al. (1997). The maximum error in the mole fraction was estimated to be about 1×10^{-3}. It results mainly from the uncertainty of the calibration curve determination.

Results and Calculations

The experimental results, that is, total vapor pressures and compositions at given temperatures and liquid compositions ($p-x-T-y$), are shown in Table 2 (ethanol + butyl methyl ether) and in Table 3 (ethanol + dipropyl ether). In these tables also activity coefficients and excess Gibbs energies calculated directly from experimental data are displayed. Vapor-phase nonidealities necessary to perform the calculations were expressed through second virial coefficients. The latter were calculated by the method of Hayden and O'Connell (1975) using a procedure taken from the monograph of Prausnitz et al. (1980). Molar volumes of pure liquid components, which were used to calculate the Poynting factors, were estimated by means of the Campbell and Thodos (1984) method.

The incomplete data sets ($p-x-T$) were correlated by means of the Redlich−Kister equations in the following form

$$G^E/\mathrm{J\cdot mol^{-1}} = x_1x_2\sum_{i=1}^{n}A_i(x_1 - x_2)^{i-1}$$

The objective function was taken as a sum of squares of residuals between experimental and calculated pressures. The number of adjustable parameters was assumed to be the highest among the sets, giving significant reduction of

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Table 1. Properties of Pure Components—Saturated Vapor Pressures (p^{sat}) and Densities (ρ)

	p^{sat}/kPa						ρ/g·cm^{-3}	
	308.15 K		323.15 K		338.15 K		298.15 K	
compound	this work	lit.	this work	lit.	this work	lit.	this work	lit.
ethanol	13.66	13.78[a]	29.34	29.49[a]	58.24	58.45[a]	0.78526	0.78509[d] 0.7852[e] 0.78493[f]
butyl methyl ether	28.26	28.41[b] 28.38[c]	50.69	50.90[b] 50.85[c]	85.53	85.78[b] 85.73[c]	0.73923	0.7393[d] 0.7394[g]
dipropyl ether	13.35	13.36[b] 13.30[c]	25.24	25.22[b] 25.14[c]	44.60	44.51[b] 44.37[c]	0.74235	0.7419[d] 0.7421[g]

[a] Ambrose and Sprake (1970). [b] Cidlinsky and Polak (1969). [c] Ambrose et al. (1976). [d] *TRC Thermodynamic Tables*. [e] Ormanoudis et al. (1991). [f] Hales and Ellender (1976). [g] Obama et al. (1985).

Table 2. Experimental Vapor Pressures (p), Vapor Mole Fractions (y_1), Activity Coefficients (γ_i), and Excess Gibbs Energies (G^E) for a Given Liquid Composition of the System [$x_1C_2H_5OH + (1 - x_1)C_4H_9OCH_3$]

x_1	p/kPa	y_1	γ_1	γ_2	G^E/J·mol^{-1}
		308.15 K			
0.0000	28.26	0.0000		1	0
0.1040	29.79	0.1332	2.8139	1.0342	352.8
0.1818	30.51	0.1995	2.4665	1.0714	565.0
0.2117	30.70	0.2145	2.2911	1.0980	638.5
0.4707	29.84	0.2983	1.3911	1.4206	874.2
0.5932	28.77	0.3436	1.2251	1.6675	841.5
0.6752	27.80	0.3836	1.1606	1.8956	789.8
0.7624	26.37	0.4586	1.1646	2.1603	766.5
0.8203	24.80	0.4867	1.0800	2.5475	592.3
0.9268	20.16	0.6562	1.0462	3.4116	337.3
0.9511	18.45	0.7311	1.0390	3.6593	255.7
0.9875	15.11	0.9062	1.0152	4.1011	83.3
1.0000	13.66	1.0000	1		0
		323.15 K			
0.0000	50.69	0.0000		1	0
0.0316	52.37	0.0592	3.3924	1.0204	156.4
0.1067	53.95	0.1597	2.7839	1.0182	336.9
0.1899	55.83	0.2426	2.4537	1.0479	559.8
0.3393	56.73	0.2990	1.7176	1.2089	829.9
0.4303	56.10	0.3317	1.4847	1.3222	884.4
0.6225	53.75	0.4030	1.1929	1.7093	838.7
0.6649	52.74	0.4334	1.1778	1.7939	818.6
0.7352	50.52	0.4902	1.1529	1.9583	759.3
0.8124	47.49	0.5284	1.0566	2.4052	562.5
0.8525	45.52	0.6058	1.1053	2.4545	585.1
0.9091	41.41	0.6677	1.0385	3.0582	365.2
0.9542	36.75	0.7751	1.0183	3.6548	206.0
0.9820	32.49	0.8956	1.0101	3.8290	91.5
1.0000	29.34	1.0000	1		0
		338.15 K			
0.0000	85.53	0.0000		1	0
0.0333	88.74	0.0695	3.2505	1.0165	154.7
0.1236	91.70	0.1735	2.2487	1.0298	353.8
0.1843	95.61	0.2558	2.3107	1.0396	523.1
0.2134	97.93	0.2666	2.1295	1.0884	640.8
0.4045	98.55	0.3598	1.5208	1.2648	870.0
0.5959	95.20	0.4399	1.2163	1.5777	846.1
0.7101	90.67	0.5018	1.1071	1.8659	711.5
0.7939	86.68	0.5597	1.0544	2.2209	580.6
0.8115	85.13	0.5802	1.0498	2.2751	546.4
0.8790	79.54	0.6477	1.0095	2.7849	371.8
0.8959	77.50	0.6761	1.0069	2.9025	329.2
0.9471	69.25	0.8066	1.0136	3.0624	202.5
0.9808	62.58	0.9113	0.9986	3.5130	63.9
1.0000	58.24	1.0000	1		0

Table 3. Experimental Vapor Pressures (p) and Vapor Mole Fractions (y_1), Activity Coefficients (γ_i) and Excess Gibbs Energies (G^E) for a Given Liquid Composition of the System [$x_1C_2H_5OH + (1 - x_1)C_3H_7OC_3H_7$]

x_1	p/kPa	y_1	γ_1	γ_2	G^E/J·mol^{-1}
		308.15 K			
0.0000	13.35	0.0000		1	0
0.0570	16.51	0.2422	5.1676	0.9941	225.7
0.1053	18.12	0.3458	4.3755	0.9935	383.3
0.1590	18.68	0.3711	3.2046	1.0477	574.8
0.1909	18.99	0.3946	2.8842	1.0659	650.5
0.2733	19.47	0.4314	2.2570	1.1433	819.3
0.3176	19.64	0.4512	2.0485	1.1856	881.2
0.4100	19.83	0.4764	1.6911	1.3213	973.1
0.4772	19.87	0.5019	1.5334	1.4218	994.0
0.5684	19.86	0.5233	1.3412	1.6479	979.9
0.7103	19.44	0.5745	1.1527	2.1465	825.6
0.7913	18.88	0.6171	1.0790	2.6056	666.2
0.8882	17.48	0.7202	1.0378	3.2962	426.2
0.9163	16.86	0.7599	1.0236	3.6467	332.1
1.0000	13.67	1.0000	1		0
		323.15 K			
0.0000	25.24	0.0000		1	0
0.0611	31.90	0.2811	5.0539	0.9654	177.2
0.0917	33.96	0.3355	4.2723	0.9827	315.1
0.1514	35.91	0.3924	3.1956	1.0178	512.8
0.1941	36.99	0.4223	2.7613	1.0501	635.6
0.2635	38.01	0.4586	2.2679	1.1073	781.4
0.3153	38.66	0.4753	1.9972	1.1744	881.8
0.4043	39.21	0.5071	1.6843	1.2869	970.1
0.4772	39.44	0.4998	1.4149	1.4966	1011.4
0.5587	39.53	0.5524	1.3375	1.5919	987.7
0.6912	39.17	0.6015	1.1655	2.0093	863.3
0.7949	38.05	0.6518	1.0660	2.5710	656.8
0.8655	36.49	0.7169	1.0318	3.0622	477.2
0.9165	34.71	0.7827	1.0113	3.6085	315.5
1.0000	29.34	1.0000	1		0
		338.15 K			
0.0000	44.60	0.0000		1	0
0.0622	56.26	0.2614	4.1293	0.9848	207.6
0.1017	60.00	0.3413	3.5044	0.9793	305.8
0.1500	64.07	0.3991	2.9601	1.0095	480.3
0.1952	66.78	0.4393	2.6059	1.0381	610.2
0.3219	70.84	0.5100	1.9416	1.1445	857.9
0.3906	72.09	0.5334	1.7018	1.2351	945.7
0.4728	72.99	0.5592	1.4913	1.3668	994.3
0.5649	73.45	0.5886	1.3210	1.5570	983.8
0.6831	73.26	0.6307	1.1664	1.9171	875.4
0.7914	71.74	0.6866	1.0720	2.4258	674.3
0.8555	69.80	0.7366	1.0342	2.8700	509.1
1.0000	58.24	1.0000	1		0

pressure deviations in comparison with those of lower number of parameters.

The values of the adjusted parameters together with the RMSDs of pressures (p), ethanol mole fractions in the vapor phase (y_1), and excess Gibbs energies (G^E) are shown in Table 4. The observed deviations cannot be treated as direct estimates of experimental accuracies, since in the optimization procedure liquid-phase compositions and temperature compositions were assumed to be error free. They are close to those of Ernst (1975) for the ethanol + dipropyl ether system at 333.15 K.

A few predictive models were used to predict measured data and hence to test the abilities of the methods. Because of strong and various types of interactions occurring in

Table 4. Results of the $p-x-T$ Correlation by Means of the Redlich−Kister Equation−Parameters (A_i) and Root Mean Squared Deviations (σ)

			σ^a		
system	T/K	A_i	p/kPa	y	G^E/J·mol^{-1}
ethanol + butyl methyl ether	308.15	3580.0; 170.27; 235.47	0.11	0.016	49
	323.15	3530.7; 235.47	0.36	0.016	49
	338.15	3391.6; 252.47	0.79	0.010	38
ethanol + dipropyl ether	308.15	3959.0; −316.78; 689.97	0.07	0.017	24
	323.15	3969.0; −253.07; 658.31	0.09	0.021	41
	333.15^b	3840.7; 73.248; 310.99	0.18	0.009	20
	338.15	3945.2; −75.316; 431.18	0.17	0.017	37

[a] $\sigma = [\sum_{i=1}^{n}(f_{\exp(i)} - f_{\mathrm{calc}(i)})^2/n]^{1/2}$. [b] Data of Ernst (1975).

Table 5. Prediction Accuracy of the Following Models: Modified UNIFAC, DISQUAC, Nitta−Chao, and Modified ERAS

		ethanol + butyl methyl ether σ^a			ethanol + dipropyl ether σ^a			
	model	308.15 K	323.15 K	338.15 K	308.15 K	323.15 K	333.15 K^b	338.15 K
p/kPa	mod UNIFAC	2.0	3.1	3.6	0.88	1.5	1.0	2.0
	DISQUAC	0.93	1.5	1.9	0.57	1.1	0.75	1.9
	Nitta−Chao	3.2	7.8	17	1.8	5.0	7.6	12
	ERAS	0.92	1.4	1.9	0.78	1.6	1.8	2.9
y_1	mod UNIFAC	0.032	0.028	0.028	0.033	0.038	0.014	0.029
	DISQUAC	0.013	0.015	0.019	0.028	0.035	0.012	0.029
	Nitta−Chao	0.042	0.066	0.074	0.045	0.047	0.061	0.066
	ERAS	0.019	0.017	0.017	0.027	0.035	0.019	0.031
G^E/J·mol^{-1}	mod UNIFAC	160	150	97	81	71	53	56
		(19)^c	(17)	(11)	(8.1)	(7.0)	(5.4)	(5.7)
	DISQUAC	90	87	55	48	52	43	54
		(10)	(10)	(6.3)	(4.8)	(5.1)	(4.4)	(5.4)
	Nitta−Chao	178	210	270	180	250	250	310
		(20)	(24)	(31)	(19)	(25)	(26)	(31)
	ERAS	95	99	49	79	80	79	86
		(11)	(11)	(5.7)	(7.9)	(8.0)	(8.0)	(8.7)

[a] $\sigma = [\sum_{i=1}^{n}(f_{\exp(i)} - f_{\mathrm{calc}(i)})^2/n]^{1/2}$. [b] Data of Ernst (1975). [c] Values in parentheses show ratios (in percentage) of the root-mean-square deviations (σ) to the maximum value of G^E; the parameters originate from Gmehling et al. (1993) (modified UNIFAC), Delcros et al. (1995) (DISQUAC), Legido et al. (1997) (Nitta−Chao), and Hofman and Casanova (1997) (modified ERAS) and from references therein.

alcohol + ether systems, such a test may be recognized as very severe. The models tested belonged to three different kinds: classical group contribution models based on rigid lattice excess Gibbs energy models as the modified UNIFAC model (Weidlich and Gmehling, 1987; Gmehling et al., 1993) and the DISQUAC method (Kehiaian et al., 1978); the group contribution equation of state of Nitta et al. (1977) (the Nitta−Chao method); and the chemical theory association model termed modified ERAS (Hofman and Casanova, 1997).

Conclusions drawn from the comparison between various predictive models cannot be definitive, as they are based on distinctly different assumptions. Nevertheless, it can be stated from the most general point of view that any predictive method is required to predict a maximum number of properties with a maximum accuracy and with a minimum number of model parameters.

The applicability of the most commonly used models, that is, the modified UNIFAC and DISQUAC models, is restricted to the nonvolume mixture properties limited to moderate pressures only. The ERAS and the Nitta−Chao models, based on equation of state models, are able to predict excess volumes and to describe some pure liquid properties such as $p-\rho-T$ data and enthalpies of vaporization into ideal gas. However, the reproducibilities of the pure compound properties have been tested in a systematic way only for the latter model (Legido et al., 1997).

The models being compared differ as to number of group parameters and their derivation. The energy interaction parameters between two groups seem to be the most important. The basic groups are alkyl, ether, and hydroxyl, but in the DISQUAC model the last two are discriminated depending on the aliphatic chain attached. This way the number of group parameters for this model considerably increases. Per each unlike group contact, a maximum of six parameters for the modified UNIFAC and the DISQUAC models is required which represent the temperature dependence of an interchange energy. For the Nitta−Chao model, interaction energies are used, and hence parameters describing interactions between like groups also must be determined. The maximum number of parameters per each contact is reduced to three which are used only if an interaction is considered to be of an associational character. On the other hand, the model has additional group structural parameters which are not used by the modified UNIFAC and the DISQUAC models.

The modified ERAS model is of special significance. With an improved chemical part it is expected to give a good representation of alcohol + ether properties even if the physical part of the model describing the nonspecific interaction is neglected. This is because of the similarity between ether and hydroxyl groups, except the ability to associate. Two parameters per each association type (i.e. standard enthalpy and standard entropy of association) were adjusted to the single sets of excess heat capacity data. Parameters pertaining to the other models were derived through the adjustment to numerous data sets of various properties.

The results of the vapor−liquid equilibria prediction are shown in Table 5. The observed best accuracy for the DISQUAC model can be easily explained by the exceptionally high number of interaction parameters used by it. In

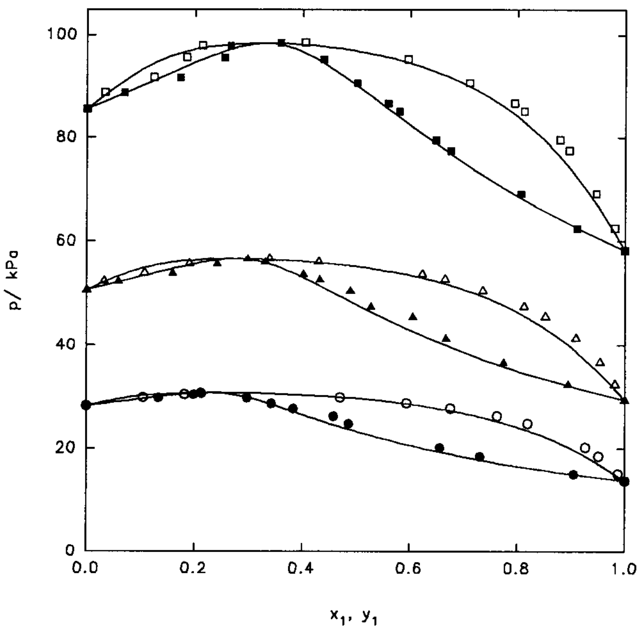

Figure 1. Vapor−liquid equilibrium isotherms for butyl methyl ether + ethanol systems. Symbols denote experimental points at (○, ●) 308.15 K; (△, ▲) 323.15 K; (□, ■) 338.15 K. Lines are predicted by the modified ERAS model.

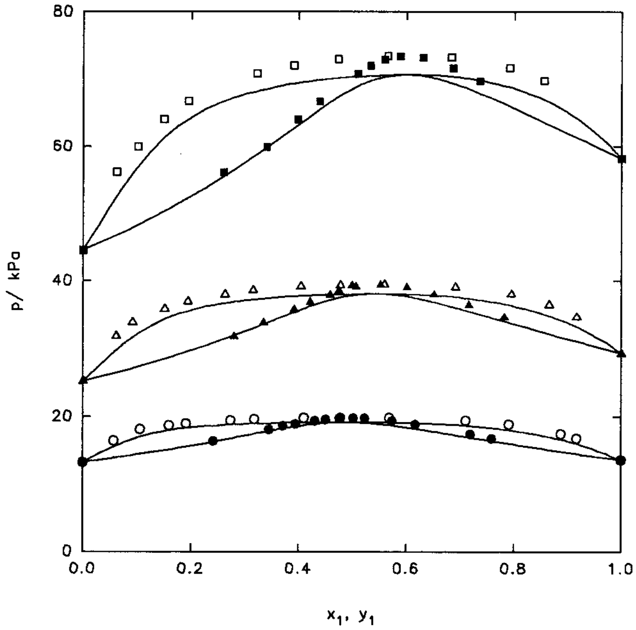

Figure 2. Vapor−liquid equilibrium isotherms for dipropyl ether + ethanol systems. Symbols denote experimental points at (○, ●) 308.15 K; (△, ▲) 323.15 K; (□, ■) 338.15 K. Lines are predicted by the modified ERAS model.

fact, its predictive character may even be questioned in favor of the correlational one. The modified ERAS model gives an only slightly worse prediction, which should be emphasized in light of the lowest number of model parameters. Figures 1 and 2 show vapor pressures as functions of liquid and vapor composition predicted by the ERAS model and plotted against the experimental values. The results are significantly better than those achieved by the modified UNIFAC method. The deviations given by the Nitta−Chao methods are always the highest ones. It seems that the model fails to describe properly associational interactions and particularly their temperature dependencies, as its parameters were fitted mainly to the 298 K data, that is at temperatures which are considerably lower than predicted vapor−liquid equilibria.

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