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Azeotropic and Heats of Mixing Data for Several Binary Organic Systems Containing 1-Methoxy-2-propanol and 2-Butoxy Ethanol

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Reliable azeotropic data have been measured for the following binary systems: 1-methoxy-2-propanol + toluene, 1-methoxy-2-propanol + cyclohexane, and 2-butoxy ethanol + decane by means of a wire band column. Additionally, molar excess enthalpies (H^E) for the four binary systems of benzene and cyclohexane with 1-methoxy-2-propanol and 2-butoxy ethanol at 313.15 K have been measured using an isothermal flow calorimeter. The azeotropic data were compared with predicted data by Modified UNIFAC (Dortmund). The H^E data measured are in good agreement with the predicted results using Modified UNIFAC (Dortmund).

Introduction

The knowledge of azeotropic points offers the most important information for the synthesis and design of distillation processes. However, the immense amount of data[1] stored in Dortmund Data Bank (more than 45 000 entries on azeotropic and zeotropic behavior) can be used not only for process synthesis (e.g., design of distillation columns, selection of the most suitable solvent for azeotropic distillation) but also for the further development of group contribution methods and for fitting reliable G^E models parameters.

In the case of G^E models,[2] a precondition for a good description of phase equilibria of multicomponent systems is the determination of reliable binary interaction parameters. In chemical industry, mainly vapor−liquid equilibria (VLE) data are used to fit the required binary parameters. However, as mentioned in previous papers,[3,4] it is recommended to fit the required interaction parameters simultaneously to all available reliable experimental data [VLE, azeotropic data, activity coefficients at infinite dilution (γ^∞), enthalpies of mixing (H^E), solid−liquid equilibria (SLE) of eutectic systems, etc.] since the parameters obtained by a simultaneous fit allow an improved representation of the real behavior across the whole composition and a large temperature range. In the Modified UNIFAC method,[5,6] different types of phase equilibria and excess properties are used for fitting simultaneously the required temperature-dependent group interaction parameters.

This paper presents azeotropic data for the binary systems 1-methoxy-2-propanol + toluene, 1-methoxy-2-propanol + cyclohexane, and 2-butoxy ethanol + decane. Additionally, excess enthalpies for binary mixtures of benzene and cyclohexane with 1-methoxy-2-propanol and 2-butoxy ethanol were measured at 313.15 K. The experimental azeotropic and H^E data were compared graphically with the results predicted by the Modified UNIFAC model using the available “oxyalcohol” main groups. For the correlation of the H^E data, a Redlich−Kister polynomial was used.

Experimental Section

Chemicals. Chemicals of high purity obtained from different suppliers were purified by vacuum distillation before their use. The purity was carefully checked by gas chromatography (GC) and Karl Fischer titration. Besides the supplier, the chemicals together with the pure component specifications are summarized in Table 1.

Apparatus and Procedure. For the measurement of azeotropic data, a commercially available microspinning wire band column with electronically controlled reflux ratio from NORMAG GmbH (Hofheim, FRG) was used to distill the mixtures as described earlier.[1] The reflux ratio is realized on the basis of vapor dividing principle. For pressures below atmospheric pressure, the desired pressure is kept constant with the help of a vacuum pump in connection with a manostat Kobold type DCM1. The temperature was determined using a resistance thermometer with an uncertainty of ± 0.1 K, and the pressure was determined by means of a sensor (Druck Limited, type PDCR) with an uncertainty of ± 0.05 kPa. For the analytical determination of the azeotropic composition, gas chromatography was used. The required factors to determine the composition from recorded peak areas were obtained using test mixtures prepared by mass with an uncertainty of ± 0.02 %. The uncertainty of the azeotropic mole fraction (y_{az}) is within ± 0.2 %. Approximately, 30 cm^3 of the binary mixture with estimated azeotropic composition was distilled at constant pressure and a small pressure drop at nearly total reflux for approximately 60 min. Then, the composition of the distillate was determined by GC. For all investigated systems, homogeneous pressure maximum azeotropes were obtained. To verify whether the system shows azeotropic (separation factor $\alpha_{12} = 1$) and not quasi-azeotropic ($\alpha_{12} \approx 1$) behavior, the experiments were always repeated starting with a different feed composition.

A commercially available isothermal flow calorimeter from Hart Scientific (model 7501) was used for the excess enthalpy measurements.[5] The calorimeter consists of two solvents pumps (ISCO, LC 2600, 260 cm^3); a thermostated flow cell; a back pressure regulator, which prevents evaporation (it is known[6] that vaporization effects may cause considerable errors at higher

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Table 1. Suppliers, Purities, Water, and Contents of the Chemicals Used

compound	supplier	CASRN[a]	purity (%)	water content (mass ppm)
1-methoxy-2-propanol	Aldrich	107-98-2	>99.9	20.0
2-butoxy ethanol	Aldrich	111-76-2	>99.8	96.4
benzene	Fisher Chemicals	71-43-2	>99.9	6.0
cyclohexane	Aldrich	110-82-7	>99.9	10.9
decane	Fluka	124-18-5	>99.9	4.9
toluene	Fluka	108-88-3	>99.9	16.4

[a] CASRN, Chemical Abstracts Service Registry Number.

Table 2. Experimental Azeotropic Data for Different Systems

	experimental data		
system	P/kPa	$y_{1,\mathrm{az}}$	T/K
1-methoxy-2-propanol (1) + toluene (2)	10.03	0.1532	317.20
	29.98	0.2081	343.06
	98.26	0.2780	379.88
1-methoxy-2-propanol (1) + cyclohexane (2)	20.04	0.0568	307.40
	60.05	0.0768	336.76
	99.71	0.0892	352.66
2-butoxy ethanol (1) + decane (2)	0.990	0.3669	320.88
	17.48	0.4609	380.89
	101.59	0.5275	435.70

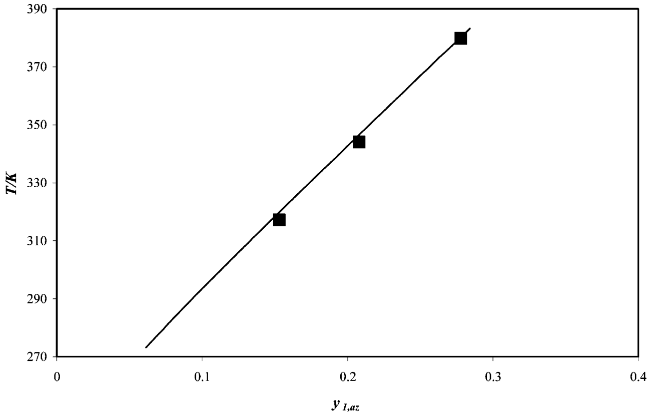

Figure 1. Experimental and predicted azeotropic data for the binary 1-methoxy-2-propanol (1) + toluene (2) system: ■, our data; —, Modified UNIFAC (Dortmund).

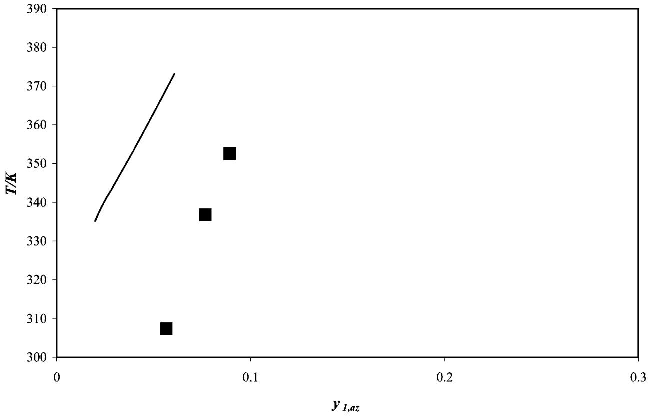

Figure 2. Experimental and predicted azeotropic data for the binary 1-methoxy-2-propanol (1) + cyclohexane (2) system: ■, our data; —, Modified UNIFAC (Dortmund).

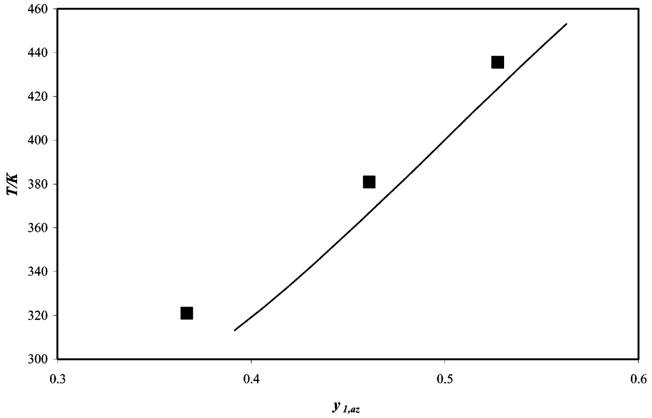

Figure 3. Experimental and predicted azeotropic data for the binary 2-butoxy ethanol (1) + decane (2) system: ■, our data; —, Modified UNIFAC (Dortmund).

Table 3. Molar Excess Enthalpies for Mixtures Containing 1-Methoxy-2-propanol and 2-Butoxy Ethanol at 313.15 K

x_1	H^E/J·mol^{-1}	x_1	H^E/J·mol^{-1}	x_1	H^E/J·mol^{-1}
1-Methoxy-2-propanol (1) + Benzene (2)					
0.0455	320.9	0.3763	808.2	0.7308	432.6
0.0914	518.8	0.4254	779.0	0.7835	351.4
0.1377	650.6	0.4750	748.5	0.8368	269.0
0.1845	736.1	0.5251	699.0	0.8906	181.7
0.2317	784.9	0.5758	641.9	0.9450	90.3
0.2794	811.2	0.6269	583.1		
0.3276	815.2	0.6786	508.6		
1-Methoxy-2-propanol (1) + Cyclohexane (2)					
0.0547	584.9	0.4232	1438.	0.7675	949.4
0.1090	891.7	0.4738	1427.	0.8149	799.8
0.1626	1093.	0.5239	1402.	0.8618	627.0
0.2158	1235.	0.5736	1345.	0.9083	439.0
0.2684	1333.	0.6227	1277.	0.9544	226.6
0.3205	1395.	0.6715	1186.		
0.3721	1426.	0.7197	1079.		
2-Butoxy Ethanol (1) + Benzene (2)					
0.0343	256.0	0.3103	682.0	0.6694	372.6
0.0698	419.8	0.3557	666.2	0.7297	303.7
0.1064	527.8	0.4029	639.2	0.7927	227.5
0.1444	608.4	0.4520	601.7	0.8586	150.4
0.1836	652.2	0.5030	556.3	0.9277	73.1
0.2243	676.9	0.5562	499.3		
0.2665	689.5	0.6116	440.9		
2-Butoxy Ethanol (1) + Cyclohexane (2)					
0.0414	417.1	0.3536	1016.	0.7111	688.7
0.0836	624.5	0.4017	1011.	0.7665	581.9
0.1265	765.7	0.4507	996.8	0.8230	459.9
0.1702	866.2	0.5007	959.3	0.8807	322.3
0.2148	929.7	0.5518	915.3	0.9397	168.1
0.2602	975.7	0.6038	853.1		
0.3065	1005.	0.6569	780.0		

temperatures) and provides the opportunity to measure H^E data also at higher pressures (up to 15 MPa). The flow cell (containing a pulsed heater, a calibration heater, a Peltier cooler, and a mixing tube wound around a copper cylinder[7]) is located in a stainless steel cylinder that is immersed in a thermostat. The power per pulse can be varied between (0.05 and 20) μJ. The exact energy per pulse is obtained by calibration using the energy dissipated from a precise resistor fixed at the cylinder of the flow cell. The temperature of the flow cell is maintained constant by adjusting the frequency of the pulsed heater to balance the cooling from the Peltier cooler and the heat effect. The temperature of the liquid pumps and the thermostat are monitored with Hart Scientific platinum resistance thermometers (model 1006 Micro-Therm) with an uncertainty of ± 0.005 K. From the recorded frequency change of the pulsed heater, the flow rate, the pure component densities, and the molar mass of the components, the molar excess enthalpies can be calculated using the energy evolved per pulse. The experimental uncertainties of this device are as follows: $\sigma(T) = 0.03$ K, $\sigma(H^E) = 2$ J·mol^{-1} + 0.01 (H^E/J·mol^{-1}), $\sigma(x_i) = 0.0001$.

Table 4. Redlich−Kister Parameters

component 1	component 2	T/K	A_1	A_2	A_3	A_4	A_5	A_6	RMSD^a/J·mol^{-1}
1-methoxy-2-propanol	benzene	313.15	2900.6	−1879.6	893.11	−593.11	1238.8	−1018.5	0.470
1-methoxy-2-propanol	cyclohexane	313.15	5676.9	−1347.3	1138.7	−180.89	2477.5	−3015.1	1.847
2-butoxy ethanol	benzene	313.15	2239.1	−1969.4	934.23	−324.27	1496.1	−1719.3	1.064
2-butoxy ethanol	cyclohexane	313.15	3866.7	−1670.3	696.22	158.97	2633.2	−3377.7	2.58

[a] RMSD $= \sqrt{(1/n)\sum_n (H^E_{\mathrm{exp}} - H^E_{\mathrm{exp}})^2}$.

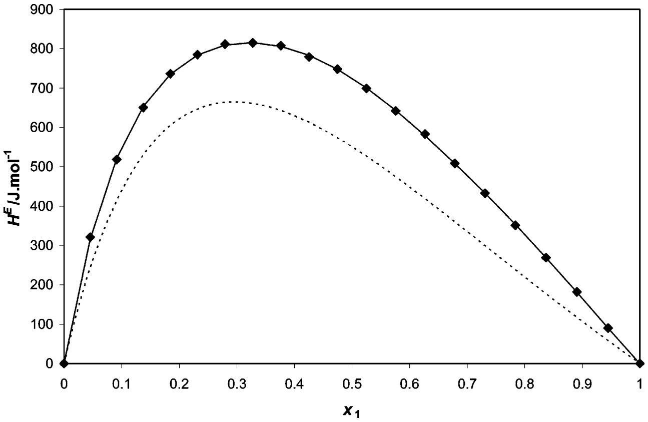

Figure 4. Experimental and correlated, respectively predicted H^E data for 1-methoxy-2-propanol (1) + benzene (2) at 313.15 K: ◆, our data; —, Redlich−Kister; - - -, Modified UNIFAC (Dortmund).

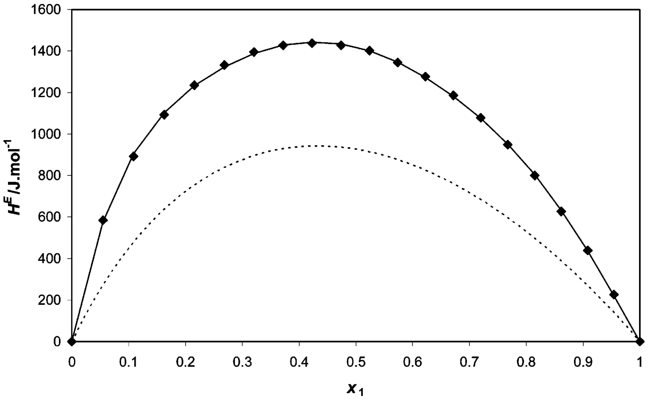

Figure 5. Experimental and correlated, respectively, predicted H^E data for 1-methoxy-2-propanol (1) + cyclohexane (2) at 313.15 K: ◆, our data; —, Redlich−Kister; - - -, Modified UNIFAC (Dortmund).

Results

The experimental azeotropic data (T, P, mole fraction) for the investigated systems 1-methoxy-2-propanol + toluene, 1-methoxy-2-propanol + cyclohexane, and 2-butoxy ethanol + decane are given in Table 2. In all cases homogeneous pressure maximum azeotropes were observed.

The experimental data for the three (alkoxyalcohol) systems were compared with the results of the group contribution method Modified UNIFAC (Dortmund) using the "oxyalcohol" main group. The results are shown in Figures 1 to 3 in the form of T−y_{az} diagrams. As can be seen, there is a good agreement between experiment and prediction for 1-methoxy-2-propanol + toluene and 2-butoxy ethanol + decane and only qualitative agreement for 1-methoxy-2-propanol + cyclohexane.

The Clausius−Clapeyron and Gibbs−Helmholtz equations give the change of the azeotropic composition with temperature. In most cases, a correct temperature dependence is predicted, which in the majority of cases depend mainly on the slope of the vapor pressure data and only to a smaller extend on the temperature dependence of the activity coefficient (partial molar excess enthalpies).[1]

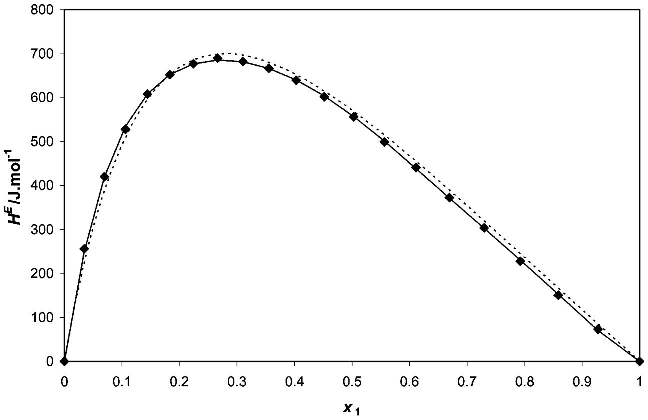

Figure 6. Experimental and correlated, respectively, predicted H^E data for 2-butoxy ethanol (1) + benzene (2) at 313.15 K: ◆, our data; —, Redlich−Kister; - - -, Modified UNIFAC (Dortmund).

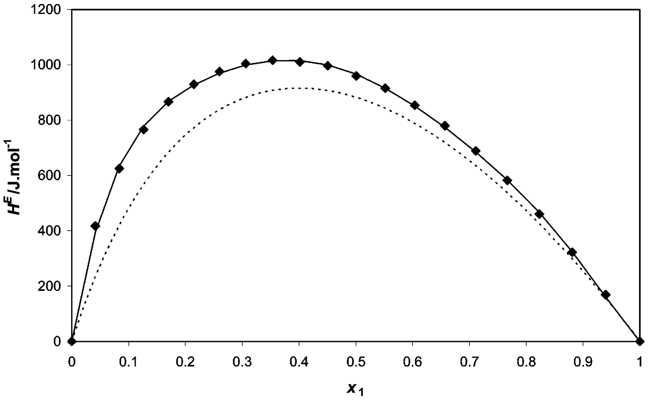

Figure 7. Experimental and correlated, respectively, predicted H^E data for 2-butoxy ethanol (1) + cyclohexane (2) at 313.15K: ◆, our data; —, Redlich−Kister; - - -, Modified UNIFAC (Dortmund).

Therefore, enthalpy of mixing measurements for systems with 1-methoxy-2-propanol and 2-butoxy ethanol were also performed. The measured excess enthalpies for the binary systems of 1-methoxy-2-propanol and 2-butoxy ethanol with benzene and cyclohexane at 313.15 K are listed in Table 3. The experimental data have been compared with the results of the group contribution method Modified UNIFAC (Dortmund) using the "oxyalcohol" main group. Additionally, the Redlich−Kister[8] equation was used to correlate the results:

$$\frac{H^E}{x_1 x_2} = \sum_j^m A_j (2x_j - 1)^{j-1} \tag{1}$$

using the following objective function:[9]

$$F = \sum_i^n \left[\left(\frac{H^E}{x_1 x_2} \right)_{\mathrm{exp}} - \left(\frac{H^E}{x_1 x_2} \right)_{\mathrm{calcd}} \right]^2 \tag{2}$$

The fitted Redlich−Kister parameters A_j together with the root-mean-square deviations (RMSD) are given in Table 4. The number of parameters used to represent the experimental data depend on the complexity of the H^E behavior, the quality of the data, and the number of data points available. The reliable and extensive data justify the use of six parameters. For all studied systems, the obtained RMSDs are within the estimated experimental uncertainty of ± 1 %.[6]

In Figures 4 to 7, the Modified UNIFAC (Dortmund) and Redlich−Kister results are compared with the experimental results. As can be seen, all systems show endothermal behavior.

In Figures 4 and 5, the H^E data for the systems 1-methoxy-2-propanol + benzene and 1-methoxy-2-propanol + cyclohexane at 313.15 K are shown. The prediction of the H^E data at 313.15 K with Modified UNIFAC (Dortmund) using the "oxyalcohol" main group is lower for both systems.

In Figures 6 and 7, the H^E data for the mixtures 2-butoxy ethanol + benzene and 2-butoxy ethanol + cyclohexane at 313.15 K are shown. The predicted H^E data at 313.15 K with Modified UNIFAC (Dortmund) using the "oxyalcohol" main group is in good agreement with the experimental data.

Conclusions

No published azeotropic or H^E data for the systems under study were found; therefore, no comparison with literature data was possible. Azeotropic data for the binary systems 1-methoxy-2-propanol + toluene, 1-methoxy-2-propanol + cyclohexane, and 2-butoxy ethanol + decane have been measured and compared with the results of the group contribution method Modified UNIFAC (Dortmund).

Additionally, excess enthalpies were measured for the binary mixtures of 1-methoxy-2-propanol and 2-butoxy ethanol with benzene and cyclohexane at 313.15 K. The H^E data have been compared with data using Modified UNIFAC (Dortmund) and correlated using the Redlich−Kister equation.

The main objective within this work was to provide new azeotropic and H^E data for systems containing the "oxyalcohol" main group. Additional phase equilibrium data measured (VLE, γ^∞, SLE of eutectic systems) for fitting the temperature-dependent G^E model, respectively group interaction parameters for systems with alkoxyalcohols, will be published soon.

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