Measurement and Correlation of Binary Vapor-Liquid Equilibria of Isomeric Butanols with 1,4-Dioxane

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Accurate Vapor-Liquid Equilibrium (VLE) data are indispensable for the design of separation equipment such as distillation columns. 1,4-dioxane, is an excellent solvent used in the manufacture of specialty chemicals, pesticides and bulk drug intermediates. In this paper, new experimental data consisting of 5 sets of PTxy data and 11 sets of PTx data, for five binary mixtures of 1,4-dioxane with isomeric butanols, have been measured in an ebulliometer. The details of the systems are presented in Tables 1a. & 1b. The measured data provide liquid activity coefficients for model correlation in order to predict VLE of multicomponent mixtures from the constituent binary model parameters. Moreover, these data are quite useful in testing the capability of group contribution models.

Table 1a: Systems for which PTxy data are measured

System	Temperature in K
2-Butanol (1)-1,4-Dioxane (2)	343.15, 363.15
1,4-Dioxane (1)-2-Methyl-1-Propanol (2)	358.15
1,4-Dioxane (1)-1-Butanol (2)	353.15, 363.15

Table 1b: Systems for which PTx data are measured

System	Temperature in K
2-Methyl-2-Propanol (1)-1,4-Dioxane (2)	323.15 K, 333.15 K, 343.15 K, 353.15 K; 26.55 kPa, 53.32 kPa, 79.97 kPa, 101.3 kPa
1,4-Dioxane (1)-2-Methyl-1-Propanol (2)	333.15 K, 368.15 K, 353.15 K

Thermodynamic consistency of 5 sets of the PTxy data was checked by the point method of Fredenslund et.al. The reliability of the PTx data has been established through the pressure residual / temperature residual vs. composition diagrams.

The experimental work on determination of PTxy and PTx data is described in detail. In the data reduction, the five popular activity coefficient models, Margules, Van Laar, Wilson, NRTL and UNIQUAC were used to obtain binary parameters. The 16 sets of PTxy and PTx data have been regressed by two optimization methods, namely, Gauss-Newton (GN) and Maximum Likelihood (MLH) to determine the binary interaction parameters of the above five models, employing suitable objective functions. In the case of PTxy data the RMSD values in vapor composition, pressure and temperature obtained by the two methods of optimization, for each model and for each set of data, are compared. In the case of PTx data, the deviations in pressure and temperature are used for comparison. Further, the vapor compositions from each set of data have been predicted by using coexistence equation and these results are compared with those obtained by the Wilson model, which is taken as the representative model for the five models studied in this work.

Moreover, the vapor compositions for the 16 sets of data have been predicted by using three versions of UNIFAC and the predictions are compared with the results calculated by Wilson and coexistence models.