Comments on "Vapor−Liquid Equilibria of Binary Mixtures Cyclopentane + Isopropyl Acetate, Isopropyl Acetate + Hexane, and Cyclopentane + Methyl Acrylate at 101.3 kPa" (Cheng, K.-W.; Chen, J.-Y.; Tang, M.; Chen, Y.-P. *J. Chem. Eng. Data* 1997, *42*, 754−757)

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Cheng et al. (1997) have recently reported vapor−liquid equilibria data for the binary mixtures of cyclopentane + isopropyl acetate, isopropyl acetate + hexane, and cyclopentane + methyl acrylate at 101.3 kPa. The data were found to be thermodynamically consistent by the Herington test and fitted using the Wilson, NRTL, and UNIQUAC models. Since the Herington test has been shown by Wisniak (1994) to be incorrect, we decided to test the results using the more stringent tests of Fredenslund et al. (1977) and Wisniak (1994), as well as the parameters given for the different models. Our results indicate that although the equilibrium data for the three systems satisfy clearly the requirements of the consistency tests, the parameters reported for the three models are incapable of returning the original data. The authors of the paper used the following objective function (OF) to determine the pertinent parameters

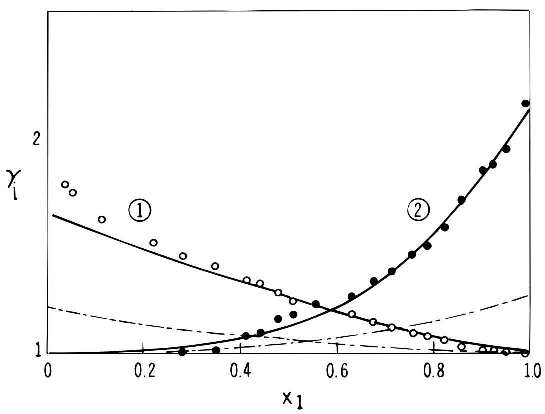

Figure 1. Activity coefficient curves for the system cyclopentane (1) + isopropyl acetate (2). Comparison of experimental data (○, ●) vs prediction by the Wilson model. (—) our parameters; (—•—) Cheng et al. parameters.

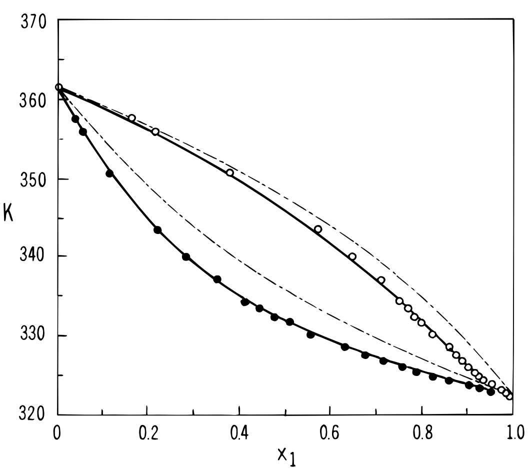

Figure 2. *T*−*x*−*y* curve for the system cyclopentane (1) + isopropyl acetate. Comparison of experimental data (○, ●) vs prediction by the Wilson model. (—) our parameters; (—•—) Cheng et al. parameters.

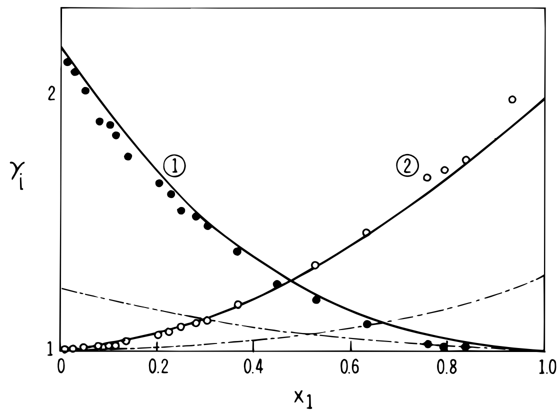

Figure 3. Activity coefficient curves for the system isopropyl acetate (1) + hexane (2). Comparison of experimental data (○, ●) vs prediction by the Wilson model. (—) our parameters; (—•—) Cheng et al. parameters.

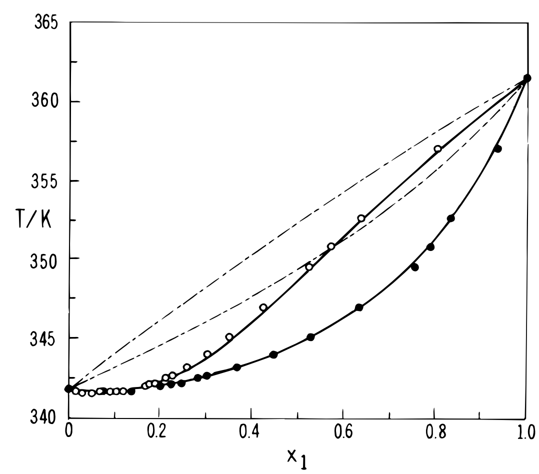

Figure 4. *T*−*x*−*y* curve for the system isopropyl acetate (1) + hexane (2). Comparison of experimental data (○, ●) vs prediction by the Wilson model. (—) our parameters; (—•—) Cheng et al. parameters.

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Table 1. Comparison between Model Parameters and Adjustment of Experimental Data

		system					
		cyclopentane (1) + isopropyl acetate (2)		isopropyl acetate (1) + hexane (2)		cyclopentane (1) + methyl methacrylate (2)	
model[a]		this work	Cheng	this work	Cheng	this work	Cheng
Wilson	$\Delta\lambda_{12}^{b}$	−51.3039	72.21	2331.468	406.76	55.0375	127.21
	$\Delta\lambda_{12}^{b}$	2277.016	443.22	49.1706	157.09	2295.91	392.22
BULBP	ΔP (%)	0.306	7.81	0.232	8.70	0.250	9.07
	Δy	0.0038	0.023	0.0056	0.036	0.0031	0.025
DEWP	ΔP (%)	0.613	7.04	0.409	8.70	0.730	7.88
	Δy	0.0048	0.030	0.0074	0.042	0.0037	0.034
BULBT	ΔT (%)	0.0956	2.559	0.073	2.91	0.0795	3.13
	Δy	0.0037	0.026	0.0056	0.037	0.0031	0.026
DEWT	ΔT (%)	0.180	2.17	0.126	2.85	0.213	3.49
	Δx	0.0045	0.030	0.0073	0.042	0.0031	0.024
NRTL[c]	$\Delta\lambda_{12}^{b}$	4341.292	926.57	1730.63	217.91	4252.237	872.23
	$\Delta\lambda_{21}^{b}$	−1924.09	−373.32	509.513	308.11	−1788.46	−322.00
BUBlP	ΔP (%)	0.382	7.48	0.678	8.53	0.207	8.74
	Δy	0.0036	0.022	0.0072	0.036	0.0031	0.022
DEWP	ΔP (%)	0.639	6.66	0.791	8.52	0.684	7.50
	Δy	0.0049	0.029	0.0105	0.041	0.0041	0.0330
BUBLT	ΔT (%)	0.119	2.47	0.213	2.84	0.0663	3.01
	Δy	0.0036	0.025	0.0073	0.037	0.0030	0.025
DEWT	ΔT (%)	0.187	2.05	0.244	2.78	0.200	2.30
	Δx	0.0046	0.029	0.010	0.041	0.0037	0.034
UNIQUAC	$\Delta\lambda_{12}^{b}$	772.11	62.96	−303.629	49.86	1308.85	60.47
	$\Delta\lambda_{21}^{b}$	−311.90	44.51	945.296	70.53	−762.57	42.77
BUBLP	ΔP (%)	0.380	5.77	0.261	9.73	0.296	5.28
	Δy	0.0036	0.017	0.0056	0.0369	0.0028	0.013
DEWP	ΔP (%)	0.656	5.02	0.395	9.71	0.714	4.21
	Δy	0.0049	0.022	0.0073	0.043	0.0033	0.021
BULBT	ΔT (%)	0.118	1.88	0.082	2.95	0.0938	1.76
	Δy	0.0036	0.019	0.0056	0.038	0.0028	0.015
DEWT	ΔT (%)	0.192	1.52	0.121	2.91	0.208	1.26
	Δx	0.0046	0.022	0.0072	0.042	0.0031	0.021

[a] All models in ln γ form. [b] Energy parameters in J·mol^{-1}. [c] $\alpha_{12} = 0.2$. [d] $\Delta P = (100/N)\sum_1^N |P_i^{exp} - P_i^{calc}|/P_i^{exp}$; $\Delta T = 100/N \sum_1^N |T_i^{exp} - T_i^{calc}|/T_i^{exp}$; $\Delta x = \sum_1^N |x_i^{exp} - x_i^{calc}|/N$; $\Delta y = \sum_1^N |y_i^{exp} - y_i^{calc}|/N$, where N is the number of experimental points. BUBLP = bubble point pressure; BUBLT = bubble point temperature; DEWP = dew point pressure; DEWT = dew point temperature.

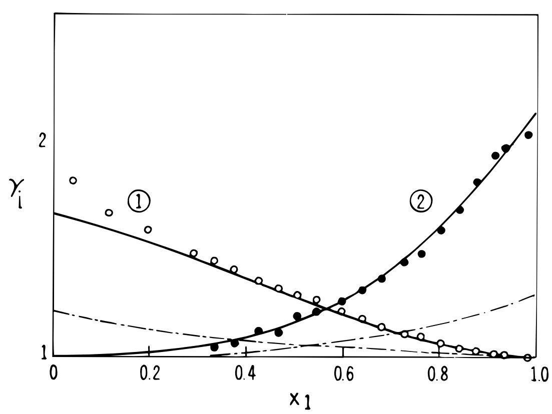

Figure 5. Activity coefficient curves for the system cyclopentane (1) + methyl methacrylate (2). Comparison of experimental data (○, ●) vs prediction by the Wilson model. (—) our parameters; (−•−) Cheng et al. parameters.

$$OF = \sum_N \sum_i \left[\frac{\gamma_i^{exp} - \gamma_i^{calc}}{\gamma_i^{exp}}\right]^2 \qquad (1)$$

We have proceeded to calculate new parameters for the three models using the alternative OF

$$OF = \sum_{i=1}^{N} 100\left[\frac{|P_i^{exp} - P_i^{calc}|}{P_i^{exp}} + \left|y_i^{exp} - y_i^{calc}\right|\right] \qquad (2)$$

We are aware that different objective functions will give different parameters, but the real test of the fitting is the capability of returning the original data. The pertinent results are indicated in Table 1, which includes also the results of Cheng et al. A more clear comparison of the difference in the quality of the fit is given in Figures 1−6 where it is seen that the parameters reported by Cheng. et al. do not reproduce the data they measured.

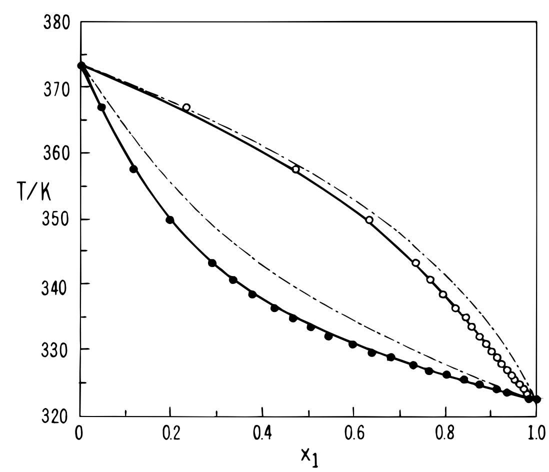

Figure 6. $T-x-y$ curve for the system cyclopentane (1) + methyl methacrylate (2). Comparison of experimental data (○, ●) vs prediction by the Wilson model. (—) our parameters; (−•−) Cheng et al. parameters.

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