

SIMULTANEOUS CORRELATION OF VAPOUR-LIQUID EQUILIBRIUM AND HEATS OF MIXING AND PREDICTION OF EXCESS HEAT CAPACITIES. THE SYSTEMS BENZENE-*n*-ALCOHOLS AND CYCLOHEXANE-*n*-ALCOHOLS

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The Wilson, the enthalpic Wilson and the Orye equations were used for the simultaneous correlation of extensive data sets on VLE and heats of mixing of eight binary systems hydrocarbon-*n*-alcohol, *viz.* benzene-methanol, -ethanol, -*n*-propanol, -*n*-butanol, cyclohexane-ethanol, -*n*-propanol, -*n*-butanol and *n*-heptane-ethanol. The expected quadratic temperature dependence of parameters of these equations makes a good simultaneous description possible of excess free enthalpy and heat of mixing as a function of temperature. The Wilson equation gives demonstrably the best description of the experimental data. All the equations were as well used to predict excess heat capacities for the systems listed and the confidence intervals were estimated for the predicted results. The comparison with experimental data for four of these systems shows that the predicted excess heat capacities are in general in good agreement with the experiment; however, the Wilson equation yielded again the best results.

The excess thermodynamic functions Gibbs free energy g^E and heat of mixing h^E are the properties of liquid mixtures that are very important for the design of distillation equipments and for the purposes of the liquid solution theories. Precise description of the temperature dependence of both these functions also makes it possible to predict the excess heat capacity, C_p^E , the quantity comparatively hard to determine experimentally. In this respect, binary mixtures of *n*-alcohols with benzene and cyclohexane have been studied experimentally in our laboratory recently. Especially a number of sets of equilibrium data¹⁻⁶, and several sets of heats of mixing^{7,8} have been measured gradually. Their complete processing comprising in addition further literature data is given just only in this work.

The problem of a good simultaneous representation of the g^E and h^E functions was investigated by a number of workers⁹⁻¹⁰. The most significant results were presented in the paper series by Nagata and Yamada¹²⁻¹⁴ who ascertained these facts: a) The Wilson equation with a quadratic dependence of energy parameters on temperature represents the experimental data on g^E and h^E generally better than the NRTL or Heil ones. b) On the assumption that the constants were obtained by correlating data on g^E and h^E lying in the range of several tens of degrees, the Wilson equation enables good prediction of excess heat capacities.

In addition to the widely well-known Wilson and NRTL equations there exist now a number of further correlation relations for excess free enthalpy whose basis is as well the local composition concept. Even if these relations are not often exploit in the literature they exhibit many good properties — they are very flexible, enable a reasonable estimate of ternary VLE from binary

data, most of them is able to describe limited miscibility and the like. To them pertain the Orye equation¹⁹ and the enthalpic Wilson equation (HMW)²⁰.

In our recent work²¹ which has dealt with the applicability of the HMW equation for correlating binary VLE we have found out that the HMW equation has in some respects even better properties than the Wilson one and gives comparable or even better results than the Wilson equation both in the binary VLE correlations and in estimating VLE from limiting activity coefficients. Therefore in this work we use besides the Wilson equation also the HMW and Orye equations for simultaneous correlation of g^E and h^E and prediction of C_p^E and compare mutually the results obtained with them.

The main aim of our work is to present in a condensed form and in a consistent way the information on excess energy functions (g^E , h^E , C_p^E) of some systems benzene-n-alcohols and cyclohexane-n-alcohols (the cyclohexane-methanol system was not treated owing to the fact that at temperatures lower than 45°C, its splitting into two liquid phases takes place) in the temperature range approximately from ambient temperature to the normal boiling points.

Correlation Equations

The equations of the local composition type, *i.e.* the Wilson, HMW and Orye ones can be summed up into the following unique form:

$$\frac{g^E}{RT} = -p \frac{x_1 x_2 \ln(A_{21} A_{12})}{(x_1 + x_2 A_{21})(x_2 + x_1 A_{12})} - q [\ln(x_1 + x_2 A_{21}) + \ln(x_2 + x_1 A_{12})], \quad (1)$$

where

$$A_{ij} \equiv \frac{v_i}{v_j} \exp\left(-\frac{\lambda_{ij} - \lambda_{jj}}{RT}\right), \quad (i \neq j); \quad (2)$$

v_i , v_j are the molar volumes of pure components and $\lambda_{ij} - \lambda_{jj}$ denote the adjustable energy parameter differences. The individual equations can be obtained on substituting for p and q according to the following scheme:

Equation	p	q
Wilson	0	1
HMW	1	0
Orye	1	1

The relations for heats of mixing and excess heat capacities are not given here explicitly because of their complexity; however, they can be obtained by applying the well-known thermodynamic relations

$$\frac{h^E}{RT} = -T \left[\frac{\partial(g^E/RT)}{\partial T} \right]_{x,P}, \quad (3)$$

$$C_p^E = (\partial h^E / \partial T)_{x,P} \quad (4)$$

to Eqs (1) and (2). As a matter of course it is necessary to specify the form of temperature dependence of $(\lambda_{ij} - \lambda_{jj})$. In this work we assume that the energy parameters are a quadratic function of temperature:

$$\lambda_{21} - \lambda_{11} = A_1 + B_1 T + C_1 T^2, \quad (5)$$

$$\lambda_{12} - \lambda_{22} = A_2 + B_2 T + C_2 T^2. \quad (6)$$

The molar volume ratio of pure components v_i/v_j is considered to be temperature independent.

Experimental Data and Their Accuracy

The activity coefficients were calculated from the data on the vapour-liquid equilibrium ($P-T-x-y$) according to the Barker relation

$$\ln \gamma_i = \ln (y_i P / x_i P_i^0) + (P - P_i^0) (B_{ii} - v_i^L) / RT + D_{ij} P (1 - y_i)^2 / RT, \quad (7)$$

where

$$D_{ij} = 2B_{ij} - B_{ii} - B_{jj} \quad (8)$$

and the excess free enthalpy

$$G \equiv g^E / RT = x_1 \ln \gamma_1 + x_2 \ln \gamma_2. \quad (9)$$

To construct statistical weights in minimization criterion and to evaluate the significance of correlation deviations it is necessary to know the possible inaccuracy of correlated quantities. It can be calculated by means of an approximate relation for the error propagation on the basis of the estimated errors of input quantities. On the assumption that the quantities x , y , P , P^0 , B_{11} , B_{22} , B_{12} are those exposed to an error and that these errors are independent and random, we can write for the variance $\sigma^2(\ln \gamma_i)$

$$\sigma^2(\ln \gamma_i) = \left(\frac{\partial \ln \gamma_i}{\partial x_i} \right)^2 \sigma^2(x_i) + \left(\frac{\partial \ln \gamma_i}{\partial y_i} \right)^2 \sigma^2(y_i) +$$

$$\begin{aligned}
 & + \left(\frac{\partial \ln \gamma_i}{\partial P} \right)^2 \sigma^2(P) + \left(\frac{\partial \ln \gamma_i}{\partial P_i^0} \right)^2 \sigma^2(P_i^0) + \\
 & + \sum_{i=1}^2 \sum_{j \geq i}^2 \left(\frac{\partial \ln \gamma_i}{\partial B_{1j}} \right)^2 \sigma^2(B_{1j}) .
 \end{aligned} \tag{10}$$

The respective derivatives can be evaluated from Eq. (7).

The errors $\sigma(x)$, $\sigma(y)$, and $\sigma(P)$ may be estimated on the basis of accuracy of measurements of the respective quantities. For calculating saturated vapour pressures of pure components we used the Antoine equation. The error in saturated vapour pressures originates therefore partly from the inaccuracy of their constants A_1 , A_2 , A_3 and partly from the error in the temperature measurement

$$\sigma^2(P^0) = \sum_{i=1}^3 \sum_{j=1}^3 \frac{\partial P^0}{\partial A_i} \frac{\partial P^0}{\partial A_j} \text{Cov}(A_i, A_j) + \left(\frac{\partial P^0}{\partial T} \right)^2 \sigma^2(T) . \tag{11}$$

For the Antoine constants taken over from the literature²² the error caused by their inaccuracy is mostly higher than that caused by the inaccuracy of temperature. Considering that we do not know the covariances $\text{Cov}(A_i, A_j)$ we approximate this term by the standard deviation of saturated vapour pressure $\sigma_w(P^0)$ given in the literature²² as

$$\sigma_w^2(P^0) = \sum_{k=1}^n (P_k^{\text{exp}} - P_k^{\text{calc}})^2 / (n - 3) . \tag{12}$$

The virial coefficients were calculated from the relation proposed by O'Connell and Prausnitz. To determine the errors of single coefficients is practically impossible. Therefore we define an effective error in virial coefficients

$$\sigma^2(B) = \sigma^2(B_{11}) = \sigma^2(B_{22}) = \sigma^2(B_{12}) , \tag{13}$$

whose value is chosen from experience.

For the overall error in $\ln \gamma_i$ holds

$$\sigma^2(\ln \gamma_i) = \sigma_x^2 + \sigma_P^2 + \sigma_{P^0}^2 + \sigma_T^2 + \sigma_B^2 , \tag{14}$$

where the individual contributions are as follows

$$\sigma_x^2 = \left(\frac{1}{x_i^2} + \frac{1}{y_i^2} \right) \sigma^2(x) , \quad \sigma^2(x) = \sigma^2(y) , \tag{15}$$

$$\sigma_P^2 = \frac{1}{P^2} \sigma^2(P), \quad (16)$$

$$\sigma_{P_1^0}^2 = \frac{1}{P_1^{0^2}} \sigma_w^2(P_1^0), \quad (17)$$

$$\sigma_T^2 = \frac{2 \cdot 303 A_2^2}{(t + A_3)^2} \sigma^2(T), \quad (18)$$

$$\sigma_B^2 = \frac{(P - P_1^0)^2 - 2P(P - P_1^0)(1 - y_1)^2 + 6P^2(1 - y_1)^4}{(RT)^2} \sigma^2(B). \quad (19)$$

The errors in the virial coefficient estimates and the error in P_1^0 induced by the vapour pressure equations are not in their character random ones but with respect to the significance of their part in the overall error they had to be inserted into the calculation. In Eqs (15)–(17) the terms considering the non-ideality of the vapour phase were neglected. According to an approximate relation for error propagation it holds for the error in G

$$\sigma^2(G) = x_1^2 \sigma^2(\ln \gamma_1) + x_2^2 \sigma^2(\ln \gamma_2) + [(\ln \gamma_1)^2 + (\ln \gamma_2)^2] \sigma^2(x). \quad (20)$$

The errors of single input quantities were, for most experimental data, estimated as follows:

$$\begin{aligned} \sigma(x) &= \sigma(y) = 0.001 \\ \sigma(P) &= 0.3 \text{ Torr} \\ \sigma(T) &= 0.02^\circ\text{C} \\ \sigma(B) &= 300 \text{ cm}^3/\text{mol}. \end{aligned} \quad (21)$$

Only some less accurate data required, however, to choose the error in pressure and especially in temperature higher:

$$\begin{aligned} \sigma(P) &= 0.5 \text{ Torr} \\ \sigma(T) &= 0.03^\circ\text{C}. \end{aligned} \quad (22)$$

The error $\sigma_w(P^0)$ differs considerably for individual substances; for some it reaches values higher than 1 Torr.

It is very difficult to determine the effect of inaccuracies in composition and in temperature on the error of experimental value of heat of mixing. As well it is problematic to determine to what sort of error the measurement of calorimetric process proper is subjected. For these reasons we choose the same overall error equal to 1 per

cent of the maximum value of $H \equiv h^E/RT$ for all measurements in the entire concentration range:

$$\sigma(H) = H_{\max}/100. \quad (23)$$

Simultaneous Correlation of g^E and h^E and Prediction of C_p^E

The best (in the statistical sense of the term) values of adjustable constants were found by minimizing the objective function S defined by the following way

$$S \equiv \sum_{k=1}^{n_G} w_k (G_k^{\text{exp}} - G_k^{\text{calc}})^2 + \sum_{l=1}^{n_H} h_l (H_l^{\text{exp}} - H_l^{\text{calc}})^2, \quad (24)$$

where w_k and h_l are weights of single points

$$w_k \equiv \frac{n_G + n_H}{n_G} \frac{1}{\sigma^2(G_k^{\text{exp}})}, \quad (25)$$

$$h_l \equiv \frac{n_G + n_H}{n_H} \frac{1}{\sigma^2(H_l^{\text{exp}})} \quad (26)$$

and n_G , n_H is number of experimental points of VLE and heat of mixing, respectively. The first factor in Eqs (25) and (26) serves the purpose to reduce weights in case of unequal number of points of VLE and heats of mixing and the second one is the statistical weight determined on the basis of errors of experimental values.

For calculating the best constants a program was made up based on a modified Marquardt algorithm²³. This procedure combines the advantages of the second-order methods (rapidity of convergence) with a high security of convergence which is peculiar to the gradient method. The program evaluates as well the matrix of variances and covariances of constants \mathbf{V} needed for the estimation of error of the calculated uncorrelated quantity (C_p^E). To calculate the matrix of the variances and covariances, the matrix of the system of normal equations \mathbf{A}_e and the value of criterion S_e for the best constants are used:

$$\mathbf{V} = \sigma^2 \mathbf{A}_e^{-1}, \quad (27)$$

$$\sigma^2 = S_e / (n - p), \quad (28)$$

where \mathbf{A}_e^{-1} is the matrix inverse to the \mathbf{A}_e one, p is the number of adjustable parameters and $n = n_G + n_H$ is the total number of points. The dispersion σ^2 is used as an overall measure of quality of the correlation carried out.

TABLE I

Summary of Correlation Results

Total deviation σ , mean absolute deviation D and deviation S_v of calculated values g^E/RT or h^E/R resp., from experimental values for single sets.

Function	Temperature or pressure	Number of points	Deviations						Ref.
			D_W	$S_{V,W}$	D_H	$S_{V,H}$	D_O	$S_{V,O}$	
benzene(1)-methanol(2)									
			$\sigma_W = 2.66$	$\sigma_H = 7.72$	$\sigma_O = 8.61$				
g^E	35°C	9	0.007	1.44	0.012	2.42	0.014	3.07	36
g^E	45°C	20	0.007	2.51	0.014	4.30	0.018	5.24	2
g^E	55°C	14	0.006	1.43	0.012	2.59	0.014	3.23	36
g^E	740 Torr	20	0.012	3.08	0.020	4.66	0.022	5.28	2
g^E	521.2 Torr	20	0.007	2.19	0.014	4.03	0.017	4.92	3
g^E	340 Torr	20	0.007	1.84	0.014	3.20	0.017	3.94	3
g^E	230.5 Torr	20	0.006	1.17	0.013	2.44	0.016	3.05	3
h^E	25°C	10	0.004	1.28	0.019	6.40	0.021	6.90	33
h^E	35°C	10	0.004	1.46	0.019	6.59	0.021	7.15	33
h^E	45°C	10	0.005	1.73	0.021	6.96	0.023	7.63	33
benzene(1)-ethanol(2)									
			$\sigma_W = 2.42$	$\sigma_H = 4.49$	$\sigma_O = 4.95$				
g^E	760 Torr	9	0.010	2.80	0.009	2.89	0.010	3.21	45
g^E	400 Torr	10	0.005	1.61	0.010	2.47	0.011	2.77	34
g^E	180 Torr	10	0.005	0.87	0.009	1.31	0.010	1.49	34
g^E	60°C	12	0.010	2.77	0.009	2.58	0.008	2.43	41
g^E	55°C	9	0.013	3.26	0.015	3.69	0.017	4.16	29
g^E	50°C	11	0.007	1.71	0.006	1.64	0.006	1.66	41
g^E	45°C	12	0.002	0.43	0.006	1.37	0.008	1.73	24
g^E	40°C	11	0.006	1.19	0.004	0.72	0.004	0.78	41
g^E	25°C	9	0.006	0.59	0.011	1.15	0.012	1.27	40
g^E	25°C	10	0.007	1.40	0.016	3.81	0.018	4.15	33
h^E	35°C	10	0.007	1.40	0.016	3.81	0.019	4.22	33
h^E	45°C	10	0.006	1.27	0.017	3.84	0.019	4.31	33
benzene(1)-propanol(2)									
			$\sigma_W = 2.87$	$\sigma_H = 4.46$	$\sigma_O = 4.88$				
g^E	760 Torr	13	0.014	3.60	0.012	3.17	0.012	3.02	42
g^E	521.2 Torr	20	0.009	2.26	0.011	2.92	0.013	3.36	4
g^E	340 Torr	20	0.008	1.83	0.011	2.40	0.012	2.74	4

TABLE I
(Continued)

Function	Temperature or pressure	Number of points	Deviations					Ref.	
			D_W	$S_{V,W}$	D_H	$S_{V,H}$	D_O		$S_{V,O}$
g^E	230.5 Torr	20	0.005	0.88	0.010	1.52	0.012	1.78	4
g^E	65°C	20	0.007	2.44	0.012	3.18	0.014	3.44	4
g^E	55°C	20	0.008	2.10	0.007	2.11	0.009	2.25	4
g^E	45°C	20	0.007	1.17	0.011	1.47	0.013	1.63	4
g^E	35°C	20	0.019	1.65	0.016	1.28	0.016	1.28	4
h^E	25°C	10	0.009	2.38	0.013	4.13	0.014	4.46	33
h^E	35°C	10	0.008	1.86	0.013	3.63	0.014	3.99	33
h^E	45°C	10	0.007	1.49	0.014	3.36	0.016	3.74	33
benzene(1)-butanol(2)									
			$\sigma_W = 2.29$	$\sigma_H = 3.46$	$\sigma_O = 3.73$				
g^E	760 Torr	18	0.005	1.36	0.012	2.56	0.014	2.86	46
g^E	521.2 Torr	19	0.007	1.65	0.011	2.29	0.012	2.52	5
g^E	340 Torr	19	0.007	1.75	0.007	1.51	0.008	1.58	5
g^E	230.5 Torr	20	0.008	0.95	0.008	1.16	0.009	1.20	5
g^E	137.1 Torr	20	0.008	0.61	0.010	0.68	0.010	0.71	5
g^E	65°C	20	0.009	1.22	0.010	1.16	0.012	1.36	5
g^E	55°C	20	0.016	1.54	0.010	0.89	0.010	0.88	5
g^E	45°C	20	0.008	0.55	0.007	0.52	0.008	0.60	5, 25
h^E	25°C	10	0.010	2.20	0.011	3.07	0.012	3.27	33
h^E	35°C	10	0.009	1.87	0.012	3.21	0.013	3.44	33
h^E	45°C	10	0.007	1.41	0.013	2.88	0.014	3.14	33
cyclohexane(1)-ethanol(2)									
			$\sigma_W = 2.99$	$\sigma_H = 4.32$	$\sigma_O = 5.09$				
g^E	5°C	7	0.007	0.21	0.010	0.34	0.012	0.40	37
g^E	20°C	7	0.006	0.36	0.011	0.74	0.014	0.88	37
g^E	25°C	9	0.023	2.60	0.023	2.36	0.022	2.28	44
g^E	35°C	7	0.007	1.66	0.012	2.11	0.015	2.36	37
g^E	50°C	7	0.002	0.60	0.008	2.06	0.011	2.68	37
g^E	65°C	7	0.003	0.73	0.007	1.74	0.010	2.27	37
g^E	760 Torr	20	0.011	3.60	0.013	4.16	0.016	4.82	30
h^E	20°C	5	0.008	1.73	0.008	2.13	0.009	2.53	47
h^E	25°C	16	0.008	1.81	0.015	3.54	0.017	4.07	7
h^E	35°C	9	0.009	1.88	0.011	2.57	0.015	3.29	14
h^E	45°C	10	0.007	1.51	0.014	3.47	0.018	4.25	14

TABLE I

(Continued)

Function	Temperature or pressure	Number of points	Deviations						Ref.
			D_W	$S_{V,W}$	D_H	$S_{V,H}$	D_O	$S_{V,O}$	
cyclohexane(1)-propanol(2)									
			$\sigma_W = 3.61$	$\sigma_H = 5.16$	$\sigma_O = 5.66$				
g^E	49-86°C	15	0.010	1.86	0.008	1.63	0.008	1.70	26
g^E	55°C	11	0.013	2.75	0.017	3.27	0.018	3.56	1
g^E	59-81°C	14	0.013	2.55	0.007	1.46	0.005	1.31	26
g^E	65°C	14	0.006	1.60	0.008	1.69	0.008	2.03	1
g^E	70°C	10	0.014	4.59	0.014	4.26	0.015	4.30	26
g^E	760 Torr	18	0.008	1.76	0.013	2.83	0.015	3.19	32
h^E	25°C	14	0.009	2.86	0.007	3.33	0.009	3.70	8
h^E	35°C	12	0.009	2.65	0.010	3.70	0.012	4.23	8
h^E	45°C	14	0.008	2.43	0.012	5.06	0.014	5.58	8
h^E	50°C	11	0.004	1.37	0.011	4.89	0.012	5.32	8
cyclohexane(1)-butanol(2)									
			$\sigma_W = 3.83$	$\sigma_H = 3.11$	$\sigma_O = 3.38$				
g^E	25°C	14	0.038	0.70	0.045	0.70	0.049	0.75	38
g^E	35°C	13	0.036	2.01	0.032	1.75	0.036	1.80	38
g^E	45°C	12	0.039	2.47	0.027	1.75	0.024	1.68	38
g^E	50°C	15	0.014	1.62	0.024	1.95	0.026	2.04	6
g^E	70°C	16	0.009	2.78	0.016	3.02	0.018	3.29	6
h^E	25°C	14	0.008	3.58	0.003	1.21	0.002	1.33	8
h^E	45°C	14	0.007	2.52	0.006	2.91	0.007	3.25	8
n-heptane(1)-ethanol(2)									
			$\sigma_W = 7.07$	$\sigma_H = 13.72$	$\sigma_O = 14.67$				
g^E	70°C	17	0.023	7.05	0.022	6.57	0.024	6.65	39
g^E	50°C	12	0.025	6.91	0.028	7.50	0.032	8.25	39
g^E	30°C	15	0.035	3.87	0.038	4.26	0.042	4.61	39
h^E	10°C	20	0.007	4.23	0.018	11.34	0.020	12.31	43
h^E	30°C	19	0.009	3.62	0.033	13.78	0.035	14.45	43
h^E	45°C	19	0.009	3.14	0.039	13.15	0.043	14.11	43
h^E	60°C	20	0.009	2.51	0.042	11.12	0.046	12.20	43
h^E	75°C	17	0.009	2.18	0.044	9.52	0.048	10.10	43

TABLE II
 Constants of Correlation Equations $A_j, B_j, C_j (\lambda_{ij} = A_j + B_j T + C_j T^2)^a$ for Eight Binary Systems

System	Equation	A_1	A_2	B_1	B_2	C_1	C_2
Benzene(1)-methanol(2)	Wilson	95.8	1 652.0	0.7580	5.5469	-0.000894	-0.015892
	HMW	26.8	- 494.4	-1.2032	7.7467	0.001154	-0.009513
	Orye	100.4	- 515.3	-2.3228	7.8283	0.002368	-0.010058
Benzene(1)-ethanol(2)	Wilson	- 96.4	2 416.8	1.8135	0.2976	-0.002951	-0.010033
	HMW	- 54.7	- 591.3	-0.2196	7.9985	0.000323	-0.011609
	Orye	60.8	- 599.6	-1.6300	8.0250	0.002136	-0.012069
Benzene(1)-propanol(2)	Wilson	- 77.5	3 049.9	2.0538	-4.5497	-0.003961	-0.003267
	HMW	-198.9	- 495.4	1.2287	7.0379	-0.002152	-0.010821
	Orye	- 99.1	- 440.6	-0.0665	6.6163	-0.000604	-0.010241
Benzene(1)-butanol(2)	Wilson	110.5	3 231.2	0.9452	-6.4072	-0.002324	-0.000776
	HMW	-218.5	- 445.7	1.7616	6.3675	-0.003082	-0.010278
	Orye	-116.2	- 363.2	0.4481	5.7353	-0.001460	-0.009173
Cyclohexane(1)-ethanol(2)	Wilson	180.0	1 078.0	2.6914	25.1768	-0.006454	-0.047290
	HMW	121.1	- 645.0	-0.8819	7.8412	0.000422	-0.009144
	Orye	217.4	- 710.2	-2.0477	8.0313	-0.001723	-0.009836
Cyclohexyne(1)-propanol(2)	Wilson	-115.4	- 722.8	2.6545	21.5824	-0.005321	-0.041995
	HMW	113.4	- 693.4	-0.9307	8.0007	0.000892	-0.010271
	Orye	191.9	- 729.0	-2.0235	8.1225	0.001994	-0.010662
Cyclohexane(1)-butanol(2)	Wilson	- 0.8	204.1	2.0723	14.4060	-0.004112	-0.030217
	HMW	93.9	- 622.5	-0.4926	7.1804	0.000234	-0.009170
	Orye	137.5	- 639.0	-1.3691	7.1968	0.000909	-0.009193
n-Heptane(1)-ethanol(2)	Wilson	312.9	827.4	1.2866	16.3848	-0.004500	-0.035944
	HMW	373.3	- 989.3	-3.2672	10.9576	0.003854	-0.013778
	Orye	536.4	- 1 129.9	- 4.9242	11.7056	0.006004	-0.015458

^a($\lambda_{ij} - \lambda_{ji}$) is expressed in cal/mol.

The survey of experimental data sets used for correlating and the comparison of results of correlations by single equations is given in Table I. To judge the quality of description of the whole system the deviation σ (Eq. (28)) is always presented. The description of single data sets can be judged partly by the mean absolute deviations in the sets given and partly by the deviations S_v defined as

$$S_v \equiv \frac{1}{m} \sum_{k=1}^m \frac{(F_k^{\text{exp}} - F_k^{\text{calc}})^2}{\sigma^2(F_k^{\text{exp}})}, \quad (29)$$

where F_k^{exp} denotes G_k^{exp} or H_k^{exp} and m is the number of points in the set. The quantity mS_v^2 has distribution χ^2 and if the data are described with experimental accuracy then the mean value of S_v^2 is equal to unity. It can be seen in the table than even in the

TABLE III
Calculated Excess Heat Capacities ($x = 0.5$) with Estimated 95 per cent Confidence Interval

Equation	C_p^E/R		Equation	C_p^E/R	
	25°C	45°C		25°C	45°C
benzene(1)-methanol(2)			cyclohexane(1)-ethanol(2)		
Wilson	1.24 ± 0.10	1.63 ± 0.14	Wilson	1.19 ± 0.15	1.79 ± 0.20
HMW	1.40 ± 0.24	1.47 ± 0.24	HMW	1.50 ± 0.25	1.55 ± 0.20
Orye	1.39 ± 0.26	1.51 ± 0.26	Orye	1.50 ± 0.24	1.59 ± 0.25
benzene(1)-ethanol(2)			cyclohexane(1)-propanol(2)		
Wilson	1.58 ± 0.10	1.98 ± 0.20	Wilson	1.21 ± 0.14	1.78 ± 0.10
HMW	1.76 ± 0.25	1.81 ± 0.25	HMW	1.44 ± 0.15	1.50 ± 0.14
Orye	1.73 ± 0.26	1.86 ± 0.24	Orye	1.40 ± 0.16	1.50 ± 0.14
benzene(1)-propanol(2)			cyclohexane(1)-butanol(2)		
Wilson	1.74 ± 0.12	2.05 ± 0.14	Wilson	1.09 ± 0.08	1.53 ± 0.16
HMW	1.87 ± 0.16	1.87 ± 0.16	HMW	1.30 ± 0.10	1.35 ± 0.10
Orye	1.83 ± 0.20	1.92 ± 0.18	Orye	1.28 ± 0.10	1.36 ± 0.10
benzene(1)-butanol(2)			n-heptane(1)-ethanol(2)		
Wilson	1.66 ± 0.10	1.90 ± 0.15	Wilson	1.20 ± 0.08	1.84 ± 0.10
HMW	1.77 ± 0.14	1.75 ± 0.15	HMW	1.71 ± 0.21	1.79 ± 0.19
Orye	1.72 ± 0.16	1.79 ± 0.16	Orye	1.68 ± 0.20	1.83 ± 0.18

TABLE IV
Comparison of Calculated Excess Heat Capacities with Experimental Data

Temperature °C/number of points	Mean absolute deviation in C_p^E/R		
	Wilson	HMW	Orye
benzene(1)-propanol(2), ref. ³⁵			
25/5	0.10	0.18	0.16
30/5	0.09	0.10	0.10
35/5	0.11	0.10	0.11
40/5	0.19	0.14	0.16
cyclohexane(1)-propanol(2), ref. ³⁵			
25/5	0.11	0.17	0.13
30/5	0.10	0.13	0.10
35/5	0.10	0.06	0.05
40/5	0.12	0.11	0.12
cyclohexane(1)-ethanol(2), ref. ³¹			
20/4	0.11	0.33	0.32
25/4	0.15	0.29	0.29
30/4	0.14	0.25	0.24
35/4	0.15	0.20	0.20
40/4	0.17	0.19	0.20
45/4	0.19	0.20	0.21
50/4	0.21	0.29	0.29
55/4	0.24	0.40	0.39
60/4	0.27	0.52	0.49
65/4	0.32	0.64	0.61
70/4	0.36	0.76	0.71
n-heptane(1)-ethanol(2) first data ref. ²⁸ , the others ref. ³¹			
25/15	0.07	0.28	0.26
20/4	0.11	0.44	0.40
25/4	0.10	0.34	0.31
30/4	0.09	0.29	0.23
35/4	0.08	0.16	0.17
40/4	0.07	0.11	0.12
45/4	0.07	0.12	0.11
50/4	0.07	0.24	0.22
55/4	0.08	0.37	0.33
60/4	0.12	0.50	0.45
65/4	0.17	0.64	0.57
70/4	0.24	0.76	0.69

best cases the data are not represented with the experimental accuracy. Further, Table I shows that with the exception of the only system the Wilson equation yielded the markedly best results and that in all the cases the HMW equation was better than the Orye one. The values of the calculated constants of single equations for individual systems are summarized as miniprint in Table II. These values of parameters were used for predicting the excess heat capacities. The computation was carried out for all the systems and for all three equations at temperatures of 25°C and 45°C. Table III presents the predicted C_p^E/R values at the point $x_1 = 0.5$ together with the estimated 95 per cent confidence interval of the value predicted (predicted value $\pm 2\sigma$). The estimation of the confidence interval was carried out according to the

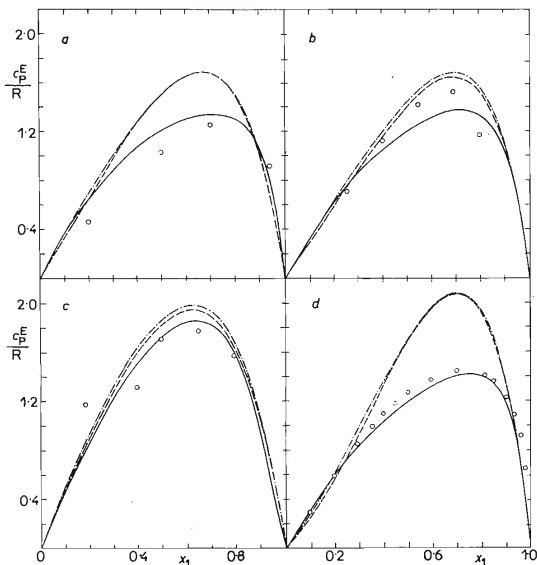


FIG. 1

Comparison of Measured and Calculated Values of Excess Heat Capacities at 25°C

Equation: ——— Wilson, - - - - Orye, - · - · HMW, circles experimental data. *a* Cyclohexane(1)-ethanol(2), *b* cyclohexane(1)-propanol(2), *c* benzene(1)-propanol(2), *d* n-heptane(1)-ethanol(2).

approximate formula for error propagation

$$\sigma(C_p^E/R) = \sum_{i=1}^p \sum_{j=1}^p \frac{\partial F}{\partial K_i} \frac{\partial F}{\partial K_j} \text{Cov}(K_i, K_j), \quad (30)$$

where K_i are the adjustable parameters, $\text{Cov}(K_i, K_j)$ the matrix elements of variances and covariances of adjustable parameters \mathbf{V} and p the number of adjustable parameters, F denotes the functional relationship for C_p^E/R .

For the four systems for which we found experimental data on excess heat capacities in the literature, we give in addition the comparison of the experimental and calculated values in Table IV and in Fig. 1. In the temperature range of experimental data on heats of mixing (usually 25–45°C) the predicted excess heat capacities are in fairly good agreement with experiment. The agreement becomes rapidly worse with increasing temperature. The best results were again reached with the Wilson equation, even though, as it can be seen from Table III, in a number of cases the results predicted in terms of single equations within the range of approximately 25°C to 45° differ practically insignificantly from the statistical point of view.

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