

LIQUID-VAPOUR EQUILIBRIUM. XLVI.*
SYSTEM CYCLOHEXANE-1-BUTANOL AT 50 and 70°C

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Isothermal liquid-vapour equilibria were measured in the system cyclohexane-1-butanol at 50 and 70°C. The results, together with the data from the literature, were employed to verify the correlation equation, allowing to express simultaneously both the temperature and the concentration dependences of the excess thermodynamic functions.

The present paper forms a part of a more extensive study whose immediate aim is to collect equilibrium data on binary systems cyclohexane-*n*-alcohols¹. It can be expected that a complete treatment of a series of this kind could result in deriving rules for the behaviour of components in the liquid-vapour phase equilibria.

System cyclohexane-1-butanol has already been measured. The extent of the hitherto performed measurements in a relatively wide temperature range directed our experiments to the measurement of isothermal equilibrium at 50 and 70°C. These measurements were used, after consistency calculations, to evaluate the excess thermodynamic functions. With respect to the fact that the up to now used calculation procedures, based above all on polynomial series with a higher number of constants, proved less adequate (mainly because of the nonsatisfactory courses of the derived relationships), we tried to draw a new kind of relation which would simultaneously describe both the concentration and the temperature dependence of excess quantities.

EXPERIMENTAL

Cyclohexane, chemically pure, was redistilled on a 40-plate column, 1-butanol, reagent grade purity, was used without further treatment. The measured physical constants are, together with the data from the literature^{2,3}, presented in Table I.

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Equilibrium data were measured on an apparatus described earlier¹. Analysis of the equilibrium mixture was carried out by measuring the refractive index with a Zeiss refractometer. Composition of the analysed mixture was determined from its refractive index by interpolating its value between the values of the weighed standard samples.

TABLE I
Physico-Chemical Properties of the Substances Used

Property	This paper	Literature	Ref.
1-Butanol			
b.p., °C 760 Torr	117.8	117.7—118.0	2
d_4^{25}	0.80603	0.80590	3
n_D^{25}	1.3974	1.3970—1.3974	2
Cyclohexane			
b.p., °C 760 Torr	80.7	80.75	2
d_4^{25}	0.7739	0.77383—0.77389	2
n_D^{25}	1.4236	1.42354—1.42358	2

RESULTS

Liquid-Vapour Equilibria

The measured equilibrium values are given in the first part of Table II for 50°C and in the first part of Table III for 70°C. Activity coefficients were calculated using the simplified relation

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

since no data were found to determine the mixed virial coefficients. The dependence of molar volumes on temperature was established for cyclohexane by interpolation of the data, given by Timmermans², that for 1-butanol by combining the data from the same work² with the equation, recommended by Benson⁴. The second virial coefficients of 1-butanol were obtained from the data, given by Fox, Marcillo, Mendez⁵ and Cox⁶, by interpolating their values into lower temperatures region. For cyclohexane they were calculated from the equation, expressing the dependence of the second virial coefficient on temperature, as suggested by Waelbrock⁷. The values of Antoine equation constants were calculated for both the components from

TABLE II
Isothermal Liquid-Vapour Equilibrium in the System Cyclohexane-1-Butanol at 50°C

x_1	y_1	P Torr	$\log \gamma_1/\gamma_2$	$(\gamma_{\text{exp}} - \gamma_{\text{calc}})$ for correlation type			
				Wilson	Laar 3	Margules 3	Margules 4
0.0065	0.1343	39.8	0.474	-0.0164	0.0022	0.0142	-0.0128
0.1446	0.7858	147.6	0.436	0.0031	0.0108	-0.0054	0.0148
0.2083	0.8374	180.5	0.392	0.0045	0.0047	-0.0141	0.0104
0.2663	0.8611	203.3	0.333	0.0009	-0.0029	-0.0207	0.0016
0.3954	0.8891	235.2	0.189	-0.0054	-0.0113	-0.0242	-0.0133
0.5558	0.9084	257.0	-0.001	-0.0080	-0.0154	-0.0144	-0.0178
0.6892	0.9199	269.0	-0.185	-0.0075	-0.0104	0.0006	-0.0111
0.7807	0.9267	274.5	-0.349	-0.0067	-0.0040	0.0112	-0.0022
0.8418	0.9343	277.7	-0.473	-0.0030	0.0040	0.0181	0.0073
0.8900	0.9383	279.6	-0.626	-0.0030	0.0066	0.0158	0.0098
0.9487	0.9512	280.3	-0.877	0.0002	0.0066	0.0051	0.0069
0.9589	0.9533	280.8	-0.958	-0.0012	0.0032	-0.0001	0.0028
0.9704	0.9582	280.2	-1.055	-0.0019	-0.0004	-0.0051	-0.0016
0.9964	0.9910	275.3	-1.300	0.0001	-0.0018	-0.0035	-0.0024
<i>Absolute mean deviation</i>				<i>0.0056</i>	<i>0.0060</i>	<i>0.0106</i>	<i>0.0085</i>

the data of Cruickshank⁸ and Brown⁹. All the data employed are summarized in Table IV.

The measured values were correlated by means of van Laar equation of the 3rd order, further by Margules equation of the 3rd and 4th order¹⁰ and by Wilson equation¹¹. The values calculated in this manner are listed in the second and further part of Tables II and III, together with the mean deviations of the measured and calculated data for molar ratios in the vapour phase. Constants of the individual correlation equations are given in Table V.

Consistency of data was checked using the relation

$$\int_0^1 \log (\gamma_1/\gamma_2) dx_1 = 0. \quad (2)$$

Proposed Expansion Series for the Calculation of Excess Free Enthalpy

When deriving the equation for the calculation of excess free enthalpy we were led by the effort to minimize the number of constants and simultaneously to preserve the possibility to express the asymmetric dependences on composition in the homogeneous region, or eventually to express a dependence with more than one extremum.

TABLE III
Isothermal Liquid-Vapour Equilibrium in the System Cyclohexan-1-Butanol at 70°C

x_1	y_1	P Torr	$\log \gamma_1/\gamma_2$	$(y_{\text{exp}} - y_{\text{calc}})$ for correlation type			
				Wilson	Laar 3	Margules 3	Margules 4
0.0213	0.2818	141.5	0.531	0.0058	0.0256	0.0312	-0.0035
0.0592	0.4844	190.5	0.449	-0.0226	-0.0039	-0.0057	-0.0227
0.1205	0.6648	282.6	0.436	-0.0016	-0.0065	-0.0051	0.0083
0.1721	0.7324	335.4	0.395	-0.0007	0.0008	-0.0140	0.0110
0.2122	0.7675	378.5	0.364	0.0005	-0.0016	-0.0168	0.0112
0.3179	0.8242	448.1	0.279	0.0030	-0.0044	-0.0164	0.0068
0.3983	0.8365	479.8	0.164	-0.0090	-0.0176	-0.0252	-0.0109
0.4509	0.8545	503.4	0.113	-0.0047	-0.0131	-0.0167	-0.0101
0.6601	0.8812	545.3	-0.142	-0.0069	-0.0090	-0.0000	-0.0129
0.7803	0.9066	561.5	-0.287	0.0052	0.0098	0.0217	0.0063
0.8860	0.9187	566.6	-0.561	0.0013	0.0091	0.0146	0.0081
0.8955	0.9174	571.0	-0.611	-0.0022	0.0053	0.0098	0.0046
0.9228	0.9237	568.3	-0.718	-0.0040	0.0018	0.0028	0.0016
0.9691	0.9475	566.7	-0.964	-0.0068	-0.0071	-0.0106	-0.0069
0.9847	0.9734	559.1	-0.969	0.0013	-0.0005	-0.0036	-0.0004
0.9833	0.9720	559.8	-0.953	0.0019	0.0001	-0.0031	0.0002
<i>Absolute mean deviation</i>				0.0048	0.0073	0.0123	0.0079

We assumed that the excess free enthalpy is only a function of composition and temperature; the pressure dependence was neglected.

Dependence of the excess free enthalpy on composition. To express generally the dependence of the excess free enthalpy on composition an expansion series is commonly used, as suggested by Redlich and Kister¹²

$$\frac{g^E/RT}{x_1x_2} = \sum_{k=0}^N A_k(x_1 - x_2)^k = \sum_{k=0}^N \tilde{A}_k(x_1 - \frac{1}{2})^k, \quad (3)$$

where A_k , \tilde{A}_k are constants, independent of composition. If further holds that $\tilde{A}_k = 2^k A_k$, where $k = 0, 1, \dots, N$. Successful application of Eq. (3) is limited by the assumption that the function is either linear or has only one single extremum in the interval $x_i \in (0, 1)$ which, moreover must lie in the close vicinity of the point $x_i = 0.5$. If this assumption is not met, then it is usually necessary to choose a too high value of N . If, however $N = 4$ or 5 which is inevitable when asymmetric dependences are to be expressed, then the polynomial on the right-hand side of Eq. (3) is no more

a smooth function and may have extrema and inflexes where they do not exist on the course of $(g^E/RT)/x_1x_2$ function. This of course results in the deterioration of all derivatives of the dependence of excess free enthalpy on composition.

Let us therefore try to find the dependence of g^E/RT on composition for asymmetric courses in the form

$$g^E/RT = f(x_1, \alpha) \sum_{k=0}^N A_k (x_1 - x_2)^k \quad [T, P] \quad (4)$$

where $f(x_1, \alpha)$ is the function of the variable $x \in \langle 0, 1 \rangle$ and of the parameter $\alpha \in (\alpha_1, \alpha_2)$ where α_1, α_2 are arbitrary and finite numbers.

TABLE IV

Molar Volumes, Second Virial Coefficients and Antoine Equation Constants of Pure Components

Component	Temperature °C	Mol. Vol. ml mol ⁻¹	2nd virial coeff. ml mol ⁻¹	Constants of Antoine equation		
				A	B	C
1-Butanol	50	94.27	-1 605	7.56483	1 416.99	184.99
	70	96.32	-1 349			
Cyclohexane	50	112.28	-1 382	6.8452	1 203.526	222.863
	70	115.24	-1 180			

TABLE V

Constants of van Laar, Margules and Wilson Equations

Temperature °C	Type and order of the series	$A_{12}(\lambda_{12})$	Constants $A_{21}(\lambda_{21})$	C_M
50	Van Laar 3	0.4685	1.2280	0.7084
	Margules 3	0.4152	1.1001	
	Margules 4	0.5276	1.1830	
	Wilson	0.7451	0.0569	
70	Van Laar 3	0.4846	1.0249	0.6342
	Margules 3	0.4614	0.9479	
	Margules 4	0.5695	1.0249	
	Wilson	0.7121	0.1271	

The function $f(x, \alpha)$ must meet the following conditions: 1. $f(0, \alpha) = 0$ for all $\alpha \in (\alpha_1, \alpha_2)$; 2. $f(1, \alpha) = 0$, for all $\alpha \in (\alpha_1, \alpha_2)$; 3. for each $x_0 \in (0, 1)$ there must just exist just one α_0 so that the function $f(x_0, \alpha_0)$ has in the interval $\langle 0, 1 \rangle$ only one extremum, lying in the point x_0 ; 4. $\lim_{x \rightarrow 0} (\partial f / \partial x) \neq 0, \pm \infty$ for all $\alpha \in (\alpha_1, \alpha_2)$ and $\lim_{x \rightarrow 1} (\partial f / \partial x) \neq 0, \pm \infty$ for all $\alpha \in (\alpha_1, \alpha_2)$.

Let us now demonstrate that the function

$$f(x, \alpha) = \exp(\alpha x) x(1 - x), \quad (5)$$

where $\alpha \in (-\infty, \infty)$ fulfills the demanded characteristics. It is evident that conditions 1, 2 and 4 are met. The third condition has still to be discussed. It holds that

$$\partial f / \partial x = -\exp(\alpha x) [\alpha x^2 + x(2 - \alpha) - 1]. \quad (6)$$

Now we have to find points in which $(\partial f / \partial x) = 0$. From equation (6) it follows that function (5), provided α has arbitrary but fixed values, can have extrema only in points defined by

$$z_1 = [\alpha - 2 + \sqrt{(\alpha^2 + 4)}] / 2\alpha, \quad z_2 = [\alpha - 2 - \sqrt{(\alpha^2 + 4)}] / 2\alpha. \quad (7)$$

The validity of the above relations can easily be demonstrated:

$$\lim_{\alpha \rightarrow -\infty} z_2 = 1, \quad dz_2/d\alpha > 0 \quad \text{for} \quad \alpha \in (-\infty, \infty) \quad (8)$$

$$\lim_{\alpha \rightarrow -\infty} z_1 = 0$$

$$\lim_{\alpha \rightarrow 0} z_1 = 0.5$$

$$\lim_{\alpha \rightarrow \infty} z_1 = 1, \quad dz_1/d\alpha > 0 \quad \text{for} \quad \alpha \in (-\infty, \infty)$$

From the first two of the above relations (8) it follows that the value z_2 does not lie within the interval $(0, 1)$ for any $\alpha \in (-\infty, \infty)$. The third, fifth and sixth of equations (8) imply that z_1 lies only within the interval $(0, 1)$ and that for any arbitrary point $x_0 \in (0, 1)$ it exist so that $z_1(\alpha_0) = x_0$. The fourth equation of the series proves that for $\alpha = 0$ equation (4) changes to (3). By this it is demonstrated that also the third of the above mentioned conditions is met.

The resulting equation to express the dependence of the excess free enthalpy on composition can be written in the form

$$g^E/RT = \exp(\alpha x_1) x_1 x_2 [A_0 + A_1(x_1 - x_2)] \quad (9)$$

or, for an asymmetric course

$$g^E/RT = \exp(\alpha x_1) x_1 x_2 [A_0 + A_1(x_1 - x_2) + A_2(x_1 - x_2)^2], \quad (10)$$

where α , A_1 are parameters, depending generally on temperature and pressure and, as far as this paper is considered, only on temperature.

Dependence of excess free enthalpy on temperature. Let us discuss the known relation between h^E and g^E in the form

$$-h^E/RT^2 = [\partial(g^E/RT)/\partial T]_{P,x}. \quad (11)$$

It is well established from experimental measurements of the heat of mixing that the quantity h^E/RT usually does not exceed the absolute value of 0.4. Then the ratio h^E/RT^2 is very small in a wide temperature range, its value being of the order of 10^{-3} and consequently the relation g^E/RT must have a distinctly linear character. It is evident that even this factor will have a negative effect when calculating the heats of mixing merely from the measurements of liquid-vapour equilibrium, moreover, if the calculations be should carried out with an adequate accuracy.

Some rather complicated dependences of g^E/RT on temperature have been described in the literature. By comparing the experimental results according to Eq. (11) it can be proved that the quantity g^E/RT cannot be a too complicated function of temperature. In a narrow temperature interval it is possible to simulate the course of g^E/RT even by some rather complicated expressions, however, such a choice makes principally an extrapolation into a wide temperature range impossible. Moreover, when suggesting more complicated expressions, considerable difficulties arise in numerical calculations which are due to the band definition of the matrices.

Taking into account this situation we were competent to consider a simple dependence of the function g^E/RT on temperature in the form

$$g^E/RT = A + BT. \quad (12)$$

This relation, however, is less suitable for the solution of our problem, for it does not give, on derivation, an expression which could be used with good results for correlating the measured values of the heats of mixing. Therefore it is more advantageous to choose another form of the function $f(T)$ which would more adequately express the linear character of the temperature dependence of the excess free enthalpy and whose first as well as higher derivatives would neither be constant nor would they change too distinctly. These characteristics are satisfied by the following functions $1/T^k$ ($k = 1, 2, \dots$), $\exp(\beta T)(A + BT)$ for $\beta \ll 1$, $\ln T$, $T \ln T$ etc. With respect to the chosen dependence of g^E/RT on composition (equations (9), (10)) the temperature dependence was taken in the form

$$g^E/RT = \exp(\beta T)(A + BT). \quad (13)$$

Dependence of the excess free enthalpy on both composition and temperature. By combining Eq. (9) or (10) with Eq. (13) it is possible to express simultaneously the dependence of the free excess enthalpy on both composition and temperature. The corresponding relations have the form

$$g^E/RT = \exp[(\alpha + \beta T)x_1] x_1 x_2 [A_0 + BT + A_1(x_1 - x_2)], \quad (14)$$

$$g^E/RT = \exp[(\alpha + \beta T)x_1] x_1 x_2 [A_0 + BT + A_1(x_1 - x_2) + A_2(x_1 - x_2)^2]. \quad (15)$$

This form of the equations (14) and (15) makes it possible to derive easily the relations for the dependence of heats of mixing and of the excess molar heat on temperature

$$h^E/RT = -T \exp[(\alpha + \beta T)x_1] x_1 x_2 [B + \beta x_1(A_0 + BT + A_1(x_1 - x_2))] \quad (16)$$

$$h^E/RT = -T \exp[(\alpha + \beta T)x_1] \cdot$$

$$\cdot x_1 x_2 [B + \beta x_1(A_0 + BT + A_1(x_1 - x_2) + A_2(x_1 - x_2)^2)], \quad (17)$$

$$C_p^E = -T \exp[(\alpha + \beta T)x_1] x_1 x_2 [D(T) + Tx_1 \beta D(T) + Tx_1 \beta B]$$

where

$$D(T) = B + \beta x_1 [A_0 + BT + A_1(x_1 - x_2) + A_2(x_1 - x_2)^2]. \quad (18)$$

Considering the fact that an asymmetric dependence of the excess quantities could be expected in the measured system cyclohexane-1-butanol, we employed relations (15), (17) and (18) to correlate the measured data. Constants α , β , A_0 , B , A_1 and A_2 were obtained by means of the method of non-linear correlation¹³. In order to improve the stability of the calculation we introduced the substitution $T^* = (T - T_{\min}) : (T_{\max} - T_{\min})$, where T_{\min} and T_{\max} are the lowest and the highest temperature of the temperature interval, respectively. In the first iteration step, the values of A_0 and B_0 were read off from the graphical plot $g^E/RT - T$ for a chosen constant composition, constants $\alpha = \beta = A_1 = A_2 = 0$. In each iteration step every non-zero constant was allowed to change by 10% at maximum.

TABLE VI

Calculation of g^E/RT Values from Experimental Data of the Liquid-Vapour Equilibrium and of Heats of Mixing

x_1	y_1	$(g^E/RT)_{\text{exp}}$	y_{calc}	$(g^E/RT)_{\text{calc}}$	$(y_{\text{exp}} - y_{\text{calc}})$	$(g^E/RT)_{\text{exp}} - (g^E/RT)_{\text{calc}}$
Temperature 50°C						
0.0065	0.1343	0.0387	0.1733	0.0090	-0.0390	0.0297
0.1446	0.7858	0.2287	0.8166	0.1868	-0.0308	0.0419
0.2083	0.8374	0.2710	0.8587	0.2579	-0.0213	0.0131
0.2663	0.8611	0.3224	0.8792	0.3147	-0.0181	0.0077
0.3954	0.8891	0.4018	0.9003	0.4085	-0.0112	-0.0067
0.5558	0.9084	0.4337	0.9098	0.4517	-0.0014	-0.0180
0.6892	0.9199	0.4086	0.9162	0.4189	0.0037	-0.0102
0.7807	0.9267	0.3554	0.9223	0.3562	0.0044	-0.0007
0.8418	0.9343	0.2959	0.9276	0.2924	0.0067	0.0034
0.8900	0.9383	0.2377	0.9337	0.2265	0.0046	0.0112
0.9487	0.9512	0.1355	0.9499	0.1216	0.0013	0.0139
0.9589	0.9533	0.1159	0.9554	0.1000	-0.0021	0.0159
0.9704	0.9582	0.0883	0.9633	0.0742	-0.0051	0.0142
0.9964	0.9910	0.0174	0.9937	0.0097	-0.0027	0.0077
Temperature 70°C						
0.0213	0.2818	0.0622	0.3051	0.0281	-0.0233	0.0341
0.0592	0.4844	0.0986	0.5494	0.0769	-0.0650	0.0216
0.1205	0.6648	0.1817	0.7087	0.1521	-0.0439	0.0296
0.1721	0.7324	0.2195	0.7708	0.2107	-0.0384	0.0088
0.2122	0.7675	0.2673	0.8001	0.2526	-0.0326	0.0147
0.3179	0.8242	0.3216	0.8409	0.3448	-0.0167	-0.0232
0.3983	0.8365	0.3876	0.8548	0.3941	-0.0183	-0.0065
0.4600	0.8545	0.3969	0.8610	0.4184	-0.0065	-0.0215
0.6601	0.8812	0.3986	0.8760	0.4070	0.0052	-0.0083
0.7803	0.9066	0.3235	0.8913	0.3317	0.0153	-0.0082
0.8860	0.9187	0.2216	0.9124	0.2142	0.0063	0.0074
0.8955	0.9174	0.2168	0.9151	0.2006	0.0023	0.0162
0.9228	0.9237	0.1699	0.9246	0.1578	-0.0009	0.0121
0.9691	0.9475	0.0851	0.9540	0.0708	-0.0065	0.0143
0.9847	0.9734	0.0488	0.9726	0.0365	0.0008	0.0122
0.9833	0.9720	0.0524	0.9707	0.0397	0.0013	0.0127

TABLE VII

Calculation of h^E/RT from the Experimental Data of the Liquid-Vapour Equilibrium and of Heats of Mixing

x_1	$(h^E/RT)_{\text{exp}}$	$(h^E/RT)_{\text{calc}}$	$(h^E/RT)_{\text{exp}} - (h^E/RT)_{\text{calc}}$
Temperature 25°C			
0.0921	0.0544	0.0656	-0.0111
0.1866	0.1061	0.1160	-0.0099
0.2194	0.1202	0.1304	-0.0102
0.2282	0.1250	0.1341	-0.0091
0.2980	0.1541	0.1608	-0.0067
0.3625	0.1799	0.1826	-0.0027
0.4075	0.1984	0.1970	0.0015
0.4279	0.2077	0.2033	0.0044
0.4382	0.2069	0.2065	0.0005
0.4640	0.2194	0.2142	0.0052
0.5777	0.2395	0.2448	-0.0053
0.5969	0.2432	0.2488	-0.0056
0.6313	0.2436	0.2547	-0.0111
0.6848	0.2392	0.2590	-0.0198
0.7239	0.2352	0.2569	-0.0217
0.7953	0.2182	0.2366	-0.0184
0.8635	0.1892	0.1906	-0.0015
0.9322	0.1416	0.1116	0.0300
0.9661	0.1069	0.0597	0.0472
Temperature 35°C			
0.050	0.0219	0.0394	-0.0175
0.100	0.0490	0.0735	-0.0245
0.200	0.1184	0.1292	-0.0108
0.300	0.1785	0.1738	0.0047
0.400	0.2289	0.2134	0.0156
0.500	0.2698	0.2511	0.0186
0.600	0.2874	0.2840	0.0034
0.700	0.2846	0.3000	-0.0154
0.800	0.2516	0.2766	-0.0250
0.900	0.1964	0.1844	0.0120
0.950	0.1566	0.1043	0.0523
Temperature 45°C			
0.050	0.0237	0.0408	-0.0171
0.100	0.0634	0.0767	-0.0132
0.200	0.1344	0.1366	-0.0021

TABLE VII
(Continued)

x_1	$(h^E/RT)_{\text{exp}}$	$(h^E/RT)_{\text{calc}}$	$(h^E/RT)_{\text{exp}} - (h^E/RT)_{\text{calc}}$
Temperature 45°C			
0.300	0.2032	0.1866	0.0166
0.400	0.2635	0.2333	0.0302
0.500	0.3021	0.2796	0.0225
0.600	0.3277	0.3217	0.0060
0.700	0.3304	0.3453	-0.0149
0.800	0.2974	0.3235	-0.0261
0.900	0.2372	0.2196	0.0176
0.950	0.1843	0.1255	0.0587

DISCUSSION

To verify the suggested relation the data were available by Smirnova and Kurtykina¹⁴ (for temperatures 25, 35 and 45°C), further the data of Ramalho and Delmas¹⁵ (for 80, 90, 100 and 110°C) and the results of our own experiments at 50 and 70°C. All these sets of data were checked graphically as to their consistency according to Eq. (2) and the compliance with condition, expressed by relations (11) and (12) was also tested. The measurements of Smirnova and Kurtykina showed the following deviations from Eq. (2): 22% at 25°C and 12% at 35 and 45°C. The data of Ramalho and Delmas¹⁵ deviate by 8% at 80°C, by 9% at 90°C, by 15% at 100°C and by 17% at 110°C. The deviation of the data presented in this paper is 3% at 50°C and 1% at 70°C (see Fig. 1).

The validity of the condition, expressed by relations (11) and (12), was determined by plotting g^E/RT versus T for chosen molar ratios in the liquid. The dependences are shown in Fig. 3. From the consistency data as well as from the probable slope of the dependence of g^E/RT on temperature we concluded that the most suitable equilibrium liquid-vapour data are those given in the present paper.

The mentioned equilibrium data together with the heats of mixing reported by Veselý and Pick¹⁶ for the temperature of 25°C and by Smirnova and Kurtykina for 35 and 45°C were used to calculate the constants of Eq. (15). From this relation the values of g^E/RT were calculated for 50 and 70°C and from Eq. (17) the values h^E/RT for the used set of data at 25, 35 and 45°C were calculated, too. Calculation was carried out not for minimum deviations of the measured and calculated molar ratios in the vapour phase, as it is usual when treating the vapour-liquid equilibrium

TABLE VIII

Estimation of the Excess Quantities of the System Cyclohexane-1-Butanol for the Temperature Range 25 to 110°C

Temperature °C	x_1	g^E/RT	h^E/RT	s^E/RT	C_p^E/R
25	0.050	0.071	0.038	-0.033	0.081
	0.100	0.138	0.070	-0.068	0.162
	0.200	0.260	0.122	-0.138	0.332
	0.300	0.358	0.162	-0.197	0.519
	0.400	0.429	0.195	-0.234	0.736
	0.500	0.467	0.225	-0.243	0.984
	0.600	0.472	0.250	-0.222	1.238
	0.700	0.438	0.260	-0.180	1.431
	0.800	0.362	0.235	-0.127	1.431
	0.900	0.226	0.153	-0.073	1.038
0.950	0.128	0.085	-0.042	0.616	
35	0.050	0.069	0.039	-0.030	0.085
	0.100	0.136	0.074	-0.063	0.171
	0.200	0.256	0.130	-0.126	0.353
	0.300	0.353	0.174	-0.179	0.562
	0.400	0.422	0.213	-0.208	0.809
	0.500	0.459	0.251	-0.208	1.097
	0.600	0.463	0.284	-0.179	1.397
	0.700	0.429	0.300	-0.129	1.631
	0.800	0.353	0.277	-0.076	1.649
	0.900	0.221	0.185	-0.036	1.210
0.950	0.125	0.104	-0.020	0.722	
45	0.050	0.068	0.041	-0.028	0.088
	0.100	0.134	0.077	-0.057	0.179
	0.200	0.251	0.137	-0.115	0.376
	0.300	0.347	0.187	-0.160	0.607
	0.400	0.415	0.233	-0.181	0.887
	0.500	0.451	0.280	-0.171	1.218
	0.600	0.453	0.322	-0.132	1.569
	0.700	0.419	0.345	-0.074	1.852
	0.800	0.344	0.324	-0.020	1.891
	0.900	0.214	0.220	0.005	1.402
0.950	0.121	0.126	0.005	0.842	
50	0.050	0.068	0.042	-0.026	0.090
	0.100	0.133	0.078	-0.054	0.183
	0.200	0.250	0.140	-0.109	0.387
	0.300	0.344	0.193	-0.150	0.630

TABLE VIII

(Continued)

Temperature °C	x_1	g^E/RT	h^E/RT	s^E/RT	C_p^E/R	
	0.400	0.411	0.244	-0.167	0.928	
	0.500	0.447	0.295	-0.152	1.282	
	0.600	0.448	0.342	-0.106	1.661	
	0.700	0.413	0.370	-0.044	1.971	
	0.800	0.338	0.349	0.011	2.022	
	0.900	0.211	0.239	0.028	1.506	
	0.950	0.119	0.137	0.018	0.907	
	70	0.050	0.065	0.045	-0.021	0.097
		0.100	0.128	0.085	-0.043	0.200
		0.200	0.240	0.156	-0.084	0.436
0.300		0.331	0.222	-0.110	0.731	
0.400		0.395	0.289	-0.106	1.105	
0.500		0.427	0.360	-0.067	1.565	
0.600		0.425	0.430	0.005	2.071	
0.700		0.388	0.478	0.090	2.504	
0.800		0.314	0.463	0.149	2.616	
0.900		0.194	0.326	0.132	1.985	
0.950	0.109	0.191	0.081	1.207		
80	0.050	0.064	0.046	-0.018	0.100	
	0.100	0.125	0.088	-0.037	0.209	
	0.200	0.236	0.165	-0.071	0.462	
	0.300	0.325	0.237	-0.088	0.785	
	0.400	0.386	0.313	-0.073	1.203	
	0.500	0.416	0.397	-0.020	1.723	
	0.600	0.412	0.480	0.068	2.302	
	0.700	0.373	0.540	0.166	2.809	
	0.800	0.299	0.529	0.229	2.960	
	0.900	0.184	0.377	0.193	2.266	
0.950	0.103	0.222	0.118	1.384		
90	0.050	0.063	0.048	-0.015	0.103	
	0.100	0.123	0.092	-0.031	0.218	
	0.200	0.231	0.173	-0.058	0.489	
	0.300	0.318	0.253	-0.065	0.842	
	0.400	0.377	0.339	-0.038	1.307	
	0.500	0.405	0.435	0.031	1.892	
	0.600	0.398	0.534	0.136	2.553	
	0.700	0.358	0.607	0.249	3.142	
0.800	0.284	0.601	0.317	3.338		

TABLE VIII
(Continued)

Temperature °C	x_1	g^E/RT	h^E/RT	s^E/RT	C_p^E/R
	0.900	0.173	0.433	0.261	2.578
	0.950	0.097	0.256	0.160	1.581
100	0.050	0.061	0.049	-0.012	0.107
	0.100	0.120	0.095	-0.025	0.227
	0.200	0.226	0.182	-0.044	0.517
	0.300	0.311	0.269	-0.041	0.903
	0.400	0.368	0.367	-0.001	1.417
	0.500	0.392	0.477	0.085	2.073
	0.600	0.383	0.591	0.209	2.824
	0.700	0.340	0.679	0.339	3.505
	0.800	0.267	0.680	0.413	3.755
	0.900	0.160	0.495	0.335	2.923
	0.950	0.089	0.295	0.206	1.800
110	0.050	0.060	0.051	-0.009	0.111
	0.100	0.118	0.099	-0.019	0.236
	0.200	0.221	0.191	-0.030	0.546
	0.300	0.304	0.287	-0.017	0.966
	0.400	0.358	0.396	0.038	1.534
	0.500	0.380	0.521	0.142	2.268
	0.600	0.366	0.653	0.287	3.117
	0.700	0.321	0.758	0.437	3.901
	0.800	0.248	0.766	0.518	4.211
	0.900	0.146	0.564	0.418	3.304
	0.950	0.081	0.337	0.256	2.044

data, but to minimize the deviations of g^E/RT and h^E/RT . The results are given in Tables VI and VII and in Figs 2 and 4. Comparison of the tabulated data with Figs 2 and 4 shows clearly the agreement of the measured values with the calculated ones, both for g^E/RT and h^E/RT . This agreement was taken as a satisfactory evidence of the validity of the correlation expression, derived in the preceding paper. Therefore it was used together with equations (17) and (18) to estimate the excess quantities in the whole concentration range for temperatures from 25 to 110°C. The results are presented in Table VIII and in Fig. 3; full lines.

Taking into account the fact that the results of equilibrium data correlation obtained up to now, either separately¹, or in combination with heats of mixing^{17,18},

did not agree better than to 25–30%, we can hold the accordance of the measured and calculated data for fairly good. For the values of g^E/RT this accordance is

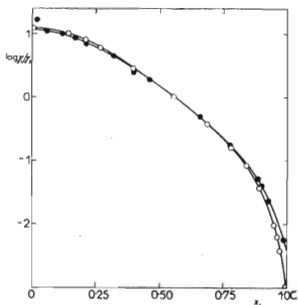


FIG. 1

Consistency of Data in the System Cyclohexane-1-Butanol for Temperatures \circ 50°C and \bullet 70°C

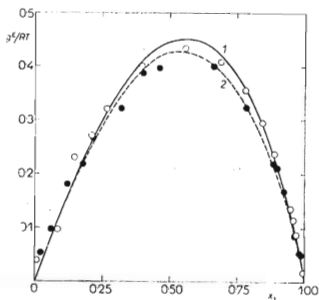
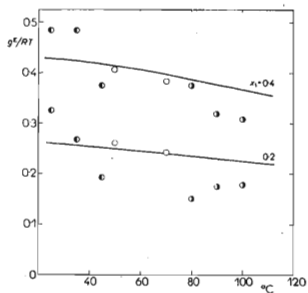
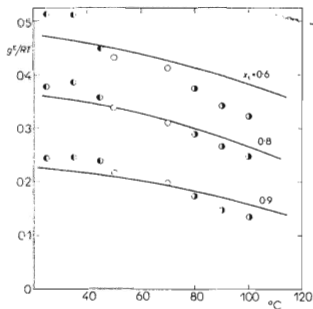


FIG. 2

Comparison of the Experimental Values (points) with the Calculated ones (curves) of g^E/RT for the Temperatures 1 50°C and 2 70°C



a



b

FIG. 3

Dependence of g^E/RT on Temperature for Chosen x (Experimental and Calculated Values) \bullet Smirnova, Kurtynina¹⁴, \circ Ramalho, Delmas¹⁵, \circ this paper.

evident in the measured region 50–70°C from Fig. 3a,b and for the values of h^E/RT from Tables VII and Fig. 4. The difference in the maximum of the dependence on composition between the calculated and the measured values^{14,16} amounts to 3%, the maximum deviation in the vicinity of the top of the curve does not exceed 8%, the error reported for the data in¹⁶ in experimental determination being 2%. The accuracy of the data in paper¹⁴ is not known. As yet no comparison could be made of the calculated excess molar heats because of the lack of experimental data. Judging merely from the analogous course of the dependence in the systems cyclohexane-ethanol and cyclohexane-1-propanol²⁰, it can be expected that the agreement might be quite satisfactory, too.

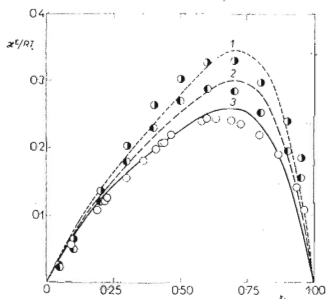


FIG. 4

Comparison of the Calculated Values (full lines) with the Experimental ones (points) of h^E/RT for the Temperatures 1 45°C, 2 35°C and 3 25°C

From the results, obtained for a considerably asymmetric course of the dependence of excess functions on composition of the system studied in the present paper one can conclude that the proposed relationship can find a wider application, particularly with respect to the extrapolation of the heats of mixing into regions in which experimental determination is very difficult. For this purpose, however, Eq. (15) must be employed for correlating other binary systems and also some other marginal problems have to be solved, mainly that of the delimitation of the extrapolation regions. This will form the subject of our next publication.

LIST OF SYMBOLS

- A, \tilde{A} constants
 B second virial coefficient of a component (l mol^{-1})
 C_M ternary constant of the 4-order Margules equation
 g^E excess molar free enthalpy (cal mol^{-1})

C_p^E	excess molar heat (cal deg mol ⁻¹)
k	addition index
P	total pressure (Torr)
P_i^0	vapour tension of pure component i (Torr)
R	gas constant
T	temperature (°K)
v	molar volume of the component (m/mol ⁻¹)
x_i	molar fraction of component i in the liquid phase
y_i	molar fraction of component i in the vapour phase
α	constant of the expansion series of the free enthalpy-composition dependence
β	constant of the expansion series of the free enthalpy-temperature dependence
γ_i	activity coefficient of component i
λ_{ii}	constants of Wilson equation
h^E	molar excess enthalpy (cal mol ⁻¹)
s^E	molar excess entropy (cal deg ⁻¹ mol ⁻¹)

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