LIQUID–VAPOUR EQUILIBRIUM
IN THE BENZENE–n-PROPANOL SYSTEM*

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Liquid–vapour equilibrium was measured at pressures of 521·2, 340, and 230·5 Torr and temperatures of 65°, 55°, 45°, and 35°C. All data sets were correlated separately by means of usually used analytic relations. The measured and selected literature data were also correlated together with the values of heats of mixing. For the correlation which would express both the concentration and the temperature dependence, the Renon equation and the modified Palmer–Smith equation were examined and their mutual comparison was carried out.

This work follows up the systematic study of equilibrium behaviour of n-alcohols with hydrocarbons which began by investigating the binary systems of alcohols with cyclohexane[1] and at the present time continues by studying the systems of n-alcohols with benzene of which the benzene–methanol system has been already published[2,3]. A direct continuation is in this work described experimental determination of liquid–vapour equilibrium in the benzene–propanol system considering that the benzene–ethanol system had been sufficiently measured in detail formerly by other athors.

EXPERIMENTAL

Preparation of pure substances. Benzene, an analytical reagent grade, was shaken with calcinated copper sulphate, then decanted and distilled with sodium on an 150 cm long column filled with stainless steel helices. The measured values of physico-chemical constants (d_4^{25} 0·8735; n_D^{25} 1·4977; n.b.p. 80·10°C; and ΔH_v^{25}·103·48 cal . g^{-1}) are in good agreement with the literature data[4,5]. n-Propanol of the analytical reagent purity was, after adding a small amount of sodium, distilled on a forty-plate bubble-cup column. The found constants (d_4^{25} 0·80347; n_D^{25} 1·3834; n.b.p. 97·24°C; and ΔH_v^{70} 174·95 cal . g^{-1}) are as well in good agreement with the published data[5-7].

Determination of the mixture compositions. The samples of equilibrium mixtures were analyzed by measuring their refractive indices at 25°C. By calibrating the dependence of refractive index on composition, it was found that the data published formerly[8] can be used as well. The attained accuracy in the composition determination of benzene–propanol mixtures was better than ± 0.001 in mole fraction.

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Apparatus. The measurement was carried out in the Gillespie equilibrium still as modified by Otsuki and Williams. The still including the temperature and/or pressure measurement and control has been described formerly[9,10]. The temperature was measured with an error of $\pm 0.01°C$ and the error in pressure did not exceed 0·4 Torr.

RESULTS

Separate Correlation of Single Sets

The experimental data are presented in Table I. The natural logarithm of activity coefficient of each component was calculated from the equation

$$\ln \gamma_i = \ln \frac{y_i P}{x_i P_i^0} + [(B_{ii} - v_i^L)(P - P_i^0) + P\delta_{ij}y_j^2]/RT, \tag{1}$$

$$\delta_{ij} = 2 B_{ij} - B_{ii} - B_{jj} \quad (j \neq i).$$

The dependence of molar volumes of pure components on temperature was considered in the linear form

$$v^L = OA + OB \cdot T. \tag{2}$$

The second virial coefficients of pure components as well as the cross virial coefficient were calculated in terms of the O'Connell and Prausnitz method[11], by using the values of critical constants taken over from the work of Kudchadker and coworkers[12]. All values needed for calculating the activity coefficients including the Antoine vapour pressure equation constants which were also taken from the literature[8,13] are summarized in Table II.

All measured data sets were first correlated separately by the Margules and the van Laar third order[14] equations and by the Wilson[15] and the Renon[16] equations. The ratio of activity coefficients was minimized. To be able to compare the values of constants of the Renon equation along the homologous series of n-alcohols the constant in the Renon eqution was chosen equal 0·47 in all cases. The results of these separate correlations are summarized in Table III as the average and standard deviations between the experimental and calculated value of mole fraction in the gas phase. In addition to it, the calculated values of constants of correlation equations are given in Table III, too. Whereas in the Margules and the van Laar equations the constants K_1 and K_2 have their usual meaning[14], in the Wilson and the Renon ones they express the difference in interaction energies $(K_i = \lambda_{ij} - \lambda_{ii},$ or $K_i = g_{ij} - g_{ii})$ so that they have the dimension of cal . mol^{-1}.

Simultaneous Data Correlation

With the aim to find a generally applicable relation for expressing the concentration and the temperature dependence of excess quantities, the Renon and the Palmer-Smith[17] equations were examined this time. Both relations would take a considerable priority in case of success because of their low number of constants.

The Renon equation was used in the same form as in case of separate correlations:

$$g^E/RT = x_1 x_2/RT \left[\frac{K_1 \exp\left(-\alpha K_1/RT\right)}{x_1 + x_2 \exp\left(-\alpha K_1/RT\right)} + \frac{K_2 \exp\left(-\alpha K_2/RT\right)}{x_1 + x_2 \exp\left(-\alpha K_2/RT\right)} \right].$$

$$(3)$$

The Palmer–Smith equation was applied in the form

$$g^E/RT = x_1 x_2 \{[m_1 M_1/(x_1 + x_2 M_1)] + [m_2 M_2/(x_2 + x_1 M_2)]\}. \tag{4}$$

The constants M_1 and M_2 are given by

$$M_i = \exp\left\{[(\Delta H_v)_{ij} - (\Delta H_v)_{ii}]/RT + m_i\right\}, \tag{5}$$

where m_i are functions of vapour pressures

$$m_i = \ln\left(P^0_{ij}/P^0_{ii}\right). \tag{6}$$

The indices ii in Eqs $(4)-(6)$ denote the property of pure component whereas the index ij denotes the property of a hypothetical solution in which only heterogeneous interactions (*i.e.* the interactions of molecules of different components) may take place. If the dependence of saturated vapour pressure on temperature is known the heat of vaporization can be estimated, *e.g.* by means of the Clausius–Clapeyron equation

$$\mathrm{d}\ln P/\mathrm{d}T = \Delta H_v/RT^2. \tag{7}$$

The data on saturated vapour pressures of pure components are known so that the values of $(\Delta H_v)_{ii}$ and P^0_{ii} can be calculated in advance and for the correlation there are only the values of heat of vaporization or saturated vapour pressure of hypothetical solution left, which is, of course, possible just for the only temperature. However, as the object of our study in this work is not only the concentration but also the temperature dependence it is necessary to express the temperature dependence of vapour pressure of the hypothetical solution. This can be done *e.g.* by the Calingaert–Davis relation

$$\log P^0_{12} = K_1 - K_2/(t + 230), \tag{8}$$

TABLE I

Experimental Data on Vapour–Liquid Equilibrium in the Benzene(1)–n-Propanol(2) System

x_1	y_1	$t, °C$	x_1	y_1	$t, °C$
		$P = 521·2$ Torr			
0·0201	0·1000	85·18	0·5478	0·7405	66·68
0·0526	0·2223	82·33	0·6082	0·7584	66·23
0·0739	0·2932	80·41	0·6890	0·7793	65·80
0·1000	0·3537	78·88	0·7599	0·8010	65·65
0·1526	0·4647	75·76	0·8293	0·8261	65·58
0·2174	0·5633	72·51	0·8590	0·8432	65·60
0·2866	0·6210	70·52	0·9193	0·8711	65·82
0·3367	0·6523	69·23	0·9478	0·9070	66·38
0·4276	0·7008	67·80	0·9800	0·9476	67·03
0·5057	0·7274	66·99	0·9942	0·9840	67·78
		$P = 340·0$ Torr			
0·0193	0·1092	74·91	0·5386	0·7808	55·22
0·0471	0·2317	72·05	0·6072	0·7986	54·67
0·0670	0·3049	70·19	0·6837	0·8094	54·21
0·0923	0·3806	68·30	0·7354	0·8297	54·01
0·1431	0·4964	64·93	0·8129	0·8395	53·85
0·2092	0·5976	61·40	0·8617	0·8542	53·85
0·2742	0·6637	59·13	0·9120	0·8771	53·97
0·3341	0·6946	57·92	0·9487	0·9016	54·29
0·4183	0·7393	56·71	0·9790	0·9458	54·90
0·5012	0·7695	55·54	0·9961	0·9840	55·50
		$P = 230·5$ Torr			
0·0162	0·1144	66·40	0·5367	0·8081	45·51
0·0425	0·2489	63·46	0·5977	0·8112	44·98
0·0628	0·3240	61·48	0·6752	0·8244	44·60
0·0867	0·4115	59·30	0·7516	0·8375	44·32
0·1336	0·5212	55·83	0·8186	0·8574	44·10
0·2035	0·6280	52·18	0·8590	0·8664	44·06
0·2667	0·6938	49·73	0·9088	0·8852	44·10
0·3234	0·7257	48·34	0·9553	0·9167	44·50
0·4034	0·7605	46·71	0·9790	0·9451	44·79
0·4900	0·7841	45·79	0·9949	0·9840	45·38

TABLE I

(*Continued*)

x_1	y_1	P, Torr	x_1	y_1	P, Torr
		$t = 65°C$			
0·0067	0·0509	203·20	0·2413	0·6127	404·40
0·0147	0·1046	213·60	0·3470	0·6736	442·80
0·0162	0·1213	222·60	0·4467	0·7111	466·20
0·0324	0·1933	247·00	0·5616	0·7525	494·00
0·0477	0·2690	253·50	0·6613	0·7718	495·80
0·0658	0·3331	273·10	0·7426	0·7912	504·00
0·0878	0·3953	295·00	0·8244	0·8226	505·90
0·1385	0·4970	338·80	0·9096	0·8655	499·70
0·1965	0·5674	377·10	0·9670	0·9280	489·60
0·2028	0·5793	381·20	0·9928	0·9771	475·40
		$t = 55°C$			
0·0105	0·0880	128·40	0·2335	0·6413	268·20
0·0306	0·2169	146·70	0·3341	0·7048	298·00
0·0365	0·2475	151·70	0·4380	0·7404	318·20
0·0514	0·3134	163·90	0·5501	0·7740	334·20
0·0648	0·3628	174·10	0·6535	0·8010	347·50
0·0891	0·4348	192·00	0·7443	0·8150	348·10
0·1071	0·4760	204·00	0·8253	0·8310	352·30
0·1324	0·5204	216·40	0·9104	0·8728	350·40
0·1860	0·5976	247·00	0·9680	0·9290	347·70
0·1950	0·6127	252·70	0·9921	0·9760	342·10
		$t = 45°C$			
0·0089	0·0986	78·50	0·1144	0·5424	136·00
0·0169	0·1575	79·80	0·1521	0·5976	152·20
0·0247	0·2119	86·60	0·9536	0·9164	240·20
0·0429	0·3214	97·30	0·9928	0·9790	226·50
0·0657	0·4192	111·30			
		$t = 35°C$			
0·0081	0·1000	44·70	0·4147	0·8027	138·60
0·0201	0·2086	49·40	0·5413	0·8300	147·50
0·0402	0·3448	57·00	0·6413	0·8470	152·30
0·0585	0·4294	64·30	0·7388	0·8605	155·10
0·1057	0·5640	78·40	0·8150	0·8673	159·50
0·1112	0·5726	82·60	0·9062	0·8920	160·10
0·1589	0·6596	95·10	0·9476	0·9139	159·10
0·1661	0·6637	102·20	0·9670	0·9340	156·70
0·2134	0·7091	108·00	0·9766	0·9484	154·80
0·2980	0·7564	120·10	0·9921	0·9773	152·00

TABLE II

Values of Pure Substance Parameters

Component	Constants of Antoine equation			Ref.	Constants of Eq. (2)		Ref.
	A	B	C		OA cm^3 . mol^{-1}	OB cm^3 . mol^{-1} K^{-1}	
Benzene	6·90565	1 211·033	220·79	13	56·23	0·1115	5
n-Propanol	7·83230	1 485·84	203·00	8	50·06	0·0840	5

TABLE III

Separate Correlation of Single Sets of Vapour–Liquid Equilibrium Data

Equation	K_1	K_2	$(y^{exp} - y^{calc})$	
			mean	standard
		$P = 760$ Torr		
Margules	1·3450	1·6702	0·016	0·017
van Laar	1·3308	1·7381	0·015	0·016
Wilson	250·5	1 465·2	0·010	0·012
Renon	451·0	1 048·1	0·013	0·014
		$P = 521·2$ Torr		
Margules	1·0661	1·6829	0·007	0·009
van Laar	1·0842	1·7985	0·006	0·007
Wilson	100·3	1 234·8	0·004	0·005
Renon	260·5	1 032·6	0·005	0·006
		$P = 340·0$ Torr		
Margules	1·0774	1·8642	0·007	0·009
van Laar	1·1004	2·1213	0·005	0·006
Wilson	53·4	1 551·8	0·003	0·004
Renon	239·5	1 248·9	0·004	0·004
		$P = 230·5$ Torr		
Margules	1·1720	1·8888	0·009	0·010
van Laar	1·1808	2·1170	0·007	0·008
Wilson	121·7	1 418·5	0·005	0·006
Renon	293·5	1 170·8	0·005	0·006

TABLE II

(*Continued*)

Component	T_k K	P_k atm	v_k cm^3 . mol^{-1}	Ref.	ω_H	μ	η	Ref.
Benzene	562·1	48·6	260	12	0·215	0	0	22
n-Propanol	536·7	51·0	218·2	12	0·201	1·68	0·57	11

TABLE III

(*Continued*)

Equation	K_1	K_2	$(y^{exp} - y^{calc})$	
			mean	standard
		$t = 65°C$		
Margules	1·2116	1·7190	0·008	0·009
van Laar	1·2114	1·8414	0·007	0·008
Wilson	165·5	1 232·2	0·004	0·005
Renon	324·6	1 032·4	0·005	0·006
		$t = 55°C$		
Margules	1·1935	1·7930	0·006	0·008
van Laar	1·1989	1·9736	0·005	0·007
Wilson	135·1	1 330·3	0·003	0·004
Renon	298·8	1 108·6	0·004	0·004
		$t = 45°C$		
Margules	1·2623	1·8713	0·008	0·010
van Laar	1·2644	2·0253	0·007	0·008
Wilson	171·5	1 292·8	0·004	0·004
Renon	330·6	1 081·9	0·005	0·005
		$t = 35°C$		
Margules	1·2378	1·9587	0·007	0·009
van Laar	1·2401	2·2335	0·005	0·007
Wilson	129·0	1 470·0	0·003	0·004
Renon	300·1	1 211·2	0·003	0·004

whose advantage consists in keeping only two constants. By applying Eq. (7) to Eq. (8) it is possible to calculate $(\Delta H_v)_{12}$, too.

For the simultaneous correlations it is necessary to use a larger number of data sets whose accuracy, unless they originate from one author, may be different. With respect to the aim to use for the intended correlation the sets taken over from the literature as well, the following tests of quality were carried out with all sets:

1) The test of consistency, for isobaric data by Herington[18] and for isothermal ones by Redlich and Kister[19]; 2) The mean deviations of the experimental and calculated values of mole fraction in the gas phase in case of the separate correlation of the set must not exceed 1%; 3) The deviation in g^E/RT computation calculated from the relation

$$\left|\Delta(g^E/RT)\right| \leqq \sum_p \left|\frac{\partial(g^E/RT)}{\partial p}\right| \left|\Delta p\right|, \tag{9}$$

where the sum is taken over all experimentally accessible parameters p from which the value of g^E/RT is calculated, should not exceed 0·02 at maximum.

These tests were satisfied by all systems measured by us and from the sets found in the literature still by the isobaric measurement[20] at 760 Torr and the isothermal one[8] at 45°C, by which the set measured by us was completed. The values of heats of mixing as a function of concentration were taken over from the paper of Mrazek and van Ness[21] who measured the heats of mixing at several temperatures with good accuracy.

When correlating, the same weights were used as those presented in one of foregoing papers[1] but as a criterion of mutual comparison of calculation accuracy, the mean

TABLE IV

Simultaneous Correlation of Vapour–Liquid Equilibrium and Heats of Mixing in the Benzene(1)–-n-Propanol(2) System by means of the Renon (*I*) and Palmer–Smith (*II*) Equations

Set	(*I*) d	(*II*) d	Set	(*I*) d	(*II*) d
K_1	438·0	7·15625	T 65	3·9	4·4
K_2	745·0	1 165·0	T 55	4·8	3·6
α	0·47	—	T 45	3·9	3·9
P 760	8·7	12·9	T 35	7·3	7·8
P 521·2	3·0	2·1	H 25	26·2	13·4
P 340	4·1	3·0	H 35	31·9	13·3
P 230·5	4·3	4·0	H 45	36·4	17·2

relative deviation related to the maximum value of function in the set considered was used according to relation

$$d = \frac{100}{\sum\limits_{I=1}^{N} w_I} \sum\limits_{I=1}^{N} \left| w_I \cdot \frac{F_I^{exp} - F_I^{calc}}{F_I^{max}} \right|, \tag{10}$$
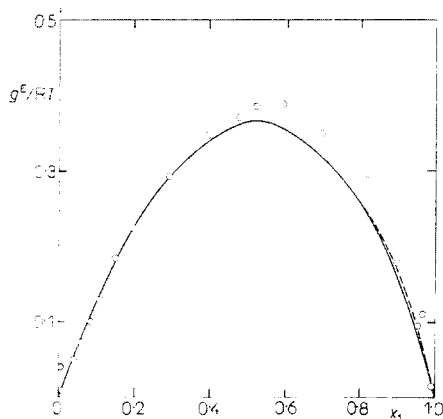
where F is g^E/RT or h^E/RT.

FIG. 1

Comparison of Simultaneous Correlation Results on Back Calculating the Dependence of g_{κ}^E/RT on x_1 at 45°C
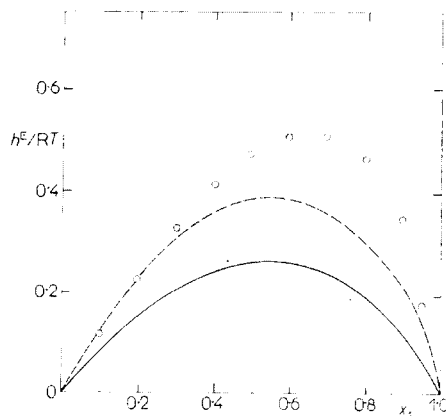———— Renon equation, – – – – Palmer–Smith equation.

FIG. 2

Comparison of Simultaneous Correlation Results on Back Calculating the Dependence of h^E/RT on x_1 at 45°C
———— Renon equation, – – – – Palmer–Smith equation.

The results of simultaneous correlations are given in Table IV. Single sets are denoted by letters (P isobaric equilibrium, T isothermal equilibrium, H heats of mixing) and by a number giving the value of pressure or temperature. In the table the constants of correlating equations are presented as well which were used in back calculations serving to determine the deviations between the experimental and calculated data.

From the results obtained it is evident that the description of the dependence of molar excess free enthalpy on composition is for both equations approximately identical but the description of the dependence of molar excess enthalpy is better on using the Palmer–Smith equation. Similar conclusions can be obtained from Figs 1 and 2, too, in which the concentration dependence of both considered thermo-

dynamic equations is demonstrated. It is evident from the figures that the determination of heats of mixing from the Renon equation is substantially worse. This fact is caused probably by a less accurate expressing of the temperature dependence which is better described by the Palmer–Smith equation.

LIST OF SYMBOLS

B	second virial coefficient	P	pressure
d	deviation defined by Eq. *(10)*	R	gas constant
g^E	molar excess free enhalpy	T	absolute temperature
h^E	molar excess enthalpy	v	molar volume
ΔH_v	heat of vaporization	w	statistical weight
K	constants of correlation equations	x	mole fraction in the liquid phase
m	constants of Eq. *(4)*	y	mole fraction in the gas phase
M	constants defined by Eq. *(5)*	α	constant of Renon equatin
OA, OB	constants of Eq. *(2)*	Δ	deviation
p	experimental parameter		

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