THE DETERMINATION OF GROUP WILSON PARAMETERS TO ACTIVITY COEFFICIENTS BY EBULLIOMETER

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Infinite dilution binary activity coefficients have been measured for 6 systems at 40 to 100°C by using an ebulliometer, to develop an accurate and rapid method for determining the group Wilson parameters for predicting liquid phase activity coefficients by "Analytical Solutions of Groups" model. The systems measured are methanol–n-heptane, ethanol–n-heptane, n-butanol–water, acetone–n-heptane, acetone–methanol, methyl ethyl ketone–water. The group Wilson parameters for any system made up of CH_2, OH, CO groups have been determined at 40 to 100°C. Predictions of infinite dilution activity coefficients and isobaric vapor-liquid equilibria made for 32 binary and 8 ternary systems involving alcohols, water, paraffins, ketones showed good agreement with observed values.

A knowledge of liquid phase activity coefficients is important for calculating vapor-liquid equilibria needed in the design of distillation equipment.

Several studies[5,17,32] have been undertaken for predicting the activity coefficients. In the "Analytical Solutions of Groups" (ASOG) model discussed by Derr and Deal[11] and Ratcliff et al.[35], based on Wilson and Deal's "Solution of Groups" model[41], the activity coefficients of a component in mixture have been predicted in terms of the group Wilson parameters associated with pairs of structural groups making up the solution. The ASOG model has had wide applicability since the number of groups making up the molecular species is much smaller than that of molecular species.

One of the limitations to a wider application of ASOG model in predicting the activity coefficients has been the lack of sets of group Wilson parameters. Therefore an accurate and rapid method for determining the group Wilson parameters is useful. Scheller et al.[37] proposed a rapid method for determining parameters by gas-liquid chromatography, but this method was restricted in practice to binary systems of groups and could not be applied to ternary or higher systems of groups.

This paper presents an accurate and rapid method for determining the group Wilson parameters by using an ebulliometer. These parameters apply not only to binary but also ternary or higher systems of groups.

Measurement of Infinite Dilution Activity Coefficients by Ebulliometer

Infinite dilution binary activity coefficients were measured accurately by using ebulliometer in the previous studies[24,25] for 23 systems at one atmospheric pressure and 2 systems at subatomospheric pressure.

In the present study, infinite dilution activity coefficients have been measured for 6 systems at 40 to 100°C for determining the group Wilson parameters of CH_2-OH, CH_2-CO and OH-CO systems. For the sake of simplicity, no distinction is made between CH_3 and CH_2 groups. The systems measured are methanol–n-heptane, ethanol–n-heptane and n-butanol–water (binary systems of groups of CH_2 and OH), acetone–n-heptane (binary system of groups of CH_2 and CO), acetone–methanol, methyl ethyl ketone–water (ternary systems of groups of CH_2, OH and CO). Details of of the ebulliometer used and the experimental procedure are not dealt with here as these were the same as in the previous paper[24]. Bubble points were measured for about 20 compositions in the case of methanol–n-heptane, ethanol–n-heptane, acetone–n-heptane and acetone–methanol, each of which is a homogeneous system, and at intervals of about 2 mol % in the dilute regions (less than 10 mol %, greater than 90 mol %). For heterogeneous systems of n-butanol–water and methyl ethyl ketone–water, bubble points were measured for about 35 compositions at intervals of 0.3 mol % in less than 3 mol %.

Table 1 Observed binary activity coefficients at infinite dilution

| System | | γ_i^∞ | t [°C] | | | | | | |
Component (1)	Component (2)		40	50	60	70	80	90	100
Methanol	n-Heptane	γ_1^∞	—	18.3	15.6	13.2	11.0	9.2	7.8
		γ_2^∞	33.9	29.7	25.2	23.6	—	—	—
Ethanol	n-Heptane	γ_1^∞	—	17.3	16.0	14.7	13.3	12.2	11.2
		γ_2^∞	13.0	12.0	11.0	10.2	9.8	—	—
n-Butanol	Water	γ_1^∞	—	—	—	59.3	57.2	55.5	54.0
		γ_2^∞	—	—	—	—	—	4.0	4.0
Acetone	n-Heptane	γ_1^∞	—	—	—	3.58	3.72	3.90	4.10
		γ_2^∞	6.35	6.13	5.91	—	—	—	—
Acetone	Methanol	γ_1^∞	2.00	1.91	1.89	1.83	—	—	—
		γ_2^∞	1.90	1.80	1.73	—	—	—	—
Methyl ethyl ketone	Water	γ_1^∞	—	—	—	26.7	28.5	30.2	31.8
		γ_2^∞	—	7.3	7.2	7.0	6.9	—	—

Material

Special grade methanol, ethanol, n-butanol, n-heptane, acetone and methyl ethyl ketone (Wako Pure Chem. Ind. Ltd.) were used. Of these methanol, n-butanol, n-heptane exceed 99.95 wt% in purity. Purities of ethanol and methyl ethyl ketone were 99.80 wt% each, and that of the acetone was 99.76 wt%.

Binary Activity Coefficients at Infinite Dilution

Measurement of infinite dilution binary activity coefficients by ebulliometer is based on calculations using Eq. (1) proposed by Gautreaux and Coates[22] and modified by Ellis and Jonah[14]:

$$\gamma_1^\infty = \left(\frac{P_2^\circ}{P_1^\circ}\right)_{T_2}\left[1-\left(\frac{d\ln P_2^\circ}{dT}\right)_{T_2}\left\{T_1-T_2+\left(\frac{\Delta T}{x_1 x_2}\right)_{x_1=0}\right\}\right]$$

$$(1)$$

where $\Delta T = T - x_1 T_1 - x_2 T_2$. The equation used for calculating γ_2^∞ is obtained by changing subscripts 1 and 2 in Eq. (1). Vapor pressures of pure materials are calculated by applying Antoine equation. Thus

$$\frac{d\ln P_i^\circ}{dT} = \frac{2.303 B_i}{(t°C+C_i)^2}$$

$$(2)$$

Table 1 shows the infinite dilution binary activity coefficients of components 1 and 2 measured at 40 to 100°C for 6 binary systems.

Determination of Parameters in Analytical Solutions of Groups Model

The model used here for Analytical Solutions of Groups is that proposed by Derr and Deal[11] and the calculation of activity coefficients is as follows:

$$\log\gamma_i = \log\gamma_i^{FH} + \log\gamma_i^G$$

$$(3)$$

where $\log\gamma_i^{FH}$ represents size contribution and $\log\gamma_i^G$ is associated with the interaction of the structural

groups of the molecule with those of its environment. The size term and the group interaction term are calculated by Eqs. (4) and (5).

$$\log\gamma_i^{FH} = \log\left(\frac{\nu_i^{FH}}{\sum_{j=1}^{n} x_j \nu_j^{FH}}\right)+0.434\left(1-\frac{\nu_i^{FH}}{\sum_{j=1}^{n} x_j \nu_j^{FH}}\right)$$

$$(4)$$

$$\log\gamma_i^G = \sum_{k}^{N} \nu_{ki}(\log\Gamma_k - \log\Gamma_k^i)$$

$$(5)$$

where ν_i^{FH} is the number of atoms (other than hydrogen) in molecular species i and ν_{ki} is the number of interacting groups of kind k in molecule i. Then Γ_k is the group activity coefficient of group k and is calculated by Wilson equation as the function of the group fraction X_k of group k.

$$X_k = \frac{\sum_{i=1}^{n} x_i \nu_{ki}}{\sum_{i=1}^{n} x_i \sum_{k}^{N} \nu_{ki}}$$

$$(6)$$

The form of the Wilson equation in representing the group activity coefficients is shown in Eq. (7). For a group, k, in a mixture consisting of N groups:

$$\log\Gamma_k = -\log\sum_{l}^{N} X_l a_{k/l} + 0.434\left[1-\sum_{l}^{N}\frac{X_l a_{l/k}}{\sum_{m}^{N} X_m a_{l/m}}\right]$$

$$(7)$$

where $a_{k/l}$, $a_{l/k}$ are group Wilson parameters and the activity coefficients are calculated by Eqs. (3) to (7) from known values of $a_{k/l}$, $a_{l/k}$. In the case of a solution containing only two groups k and l, Eq. (7) takes the simple form.

$$\log\Gamma_k = -\log(X_k + X_l a_{k/l}) + 0.434\left[1-\frac{X_k}{X_k+X_l a_{k/l}} - \frac{X_l a_{l/k}}{X_k a_{l/k}+X_l}\right]$$

$$(8)$$

Method of determining the group Wilson param-

Table 2 Constants m and n in Eq. (10) $(40 \sim 100°C)$

l \ k	CH$_2$ m	CH$_2$ n	OH m	OH n	CO m	CO n
CH$_2$	0	0	-0.4962	-11.2	2.5622	-920.9
OH	0.6007	-767.1	0	0	-0.4943	106.0
CO	-2.3979	479.8	0.2349	-121.8	0	0

eters by means of the infinite dilution activity coefficients is given below. Defining

$$F_{obj.} = \left[\sum_{d=1}^{s} \sum_{i=1}^{n} (\log \gamma_{i,obs.}^G - \log \gamma_{i,cal.}^G)_d^2 \right]^{\infty} \qquad (9)$$

where d denotes the dth observed point, and $F_{obj.}$ is a function of the group Wilson parameters only. The required parameters are calculated by an iteration method. As for the calculation, it is carried out as follows: First, the group Wilson parameters for the binary systems of groups of CH$_2$ and OH are determined on the basis of the infinite dilution activity coefficients of methanol–n-heptane, ethanol–n-heptane, n-butanol–water (Table 1), and of methanol–water, ethanol–water (25–100°C) and n-propanol–water (760 mmHg) discussed in the previous paper[24]. The water molecule is treated as 1.6 interaction hydroxyl groups, this value being the same as that used by Scheller[36]. The group Wilson parameters for the binary systems of groups of CH$_2$ and CO are hereafter calculated on the basis of the infinite dilution activity coefficients for acetone–n-heptane (Table 1). Group Wilson parameters for the binary systems of groups of OH and CO are calculated on the basis of the infinite dilution activity coefficients of acetone–methanol, methyl ethyl ketone–water (Table 1) and also of acetone–water (760 mmHg) of the previous paper[25]. As these are ternary systems of groups of CH$_2$, OH, CO and the number of the group Wilson parameters in $F_{obj.}$ is six, $a_{OH/CO}$, $a_{CO/OH}$ are calculated by using known values of $a_{CH_2/OH}$, a_{OH/CH_2}, $a_{CH_2/CO}$, a_{CO/CH_2}.

Fig. 1 shows group Wilson parameters determined at 40, 60, 80 and 100°C, plotted against the temperature. As is evident from the figure, the logarithms of group Wilson parameters are inversely proportional to the absolute temperature in the temperature range in this work. Therefore

$$\log a_{k/l} = m + n/T \qquad (10)$$

where m and n are constants with respect to group pairs. Table 2 shows the constants m and n for any system made up of CH$_2$, OH, CO groups. In Fig. 1, the group Wilson parameters given by Derr and Deal[11] are shown by dotted lines.

Prediction of Activity Coefficients at Infinite Dilution

Prediction of the binary and ternary activity coefficients at infinite dilution has been tried as the
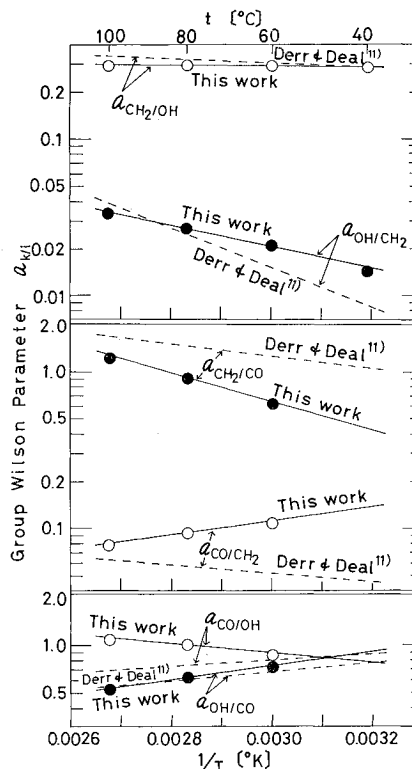

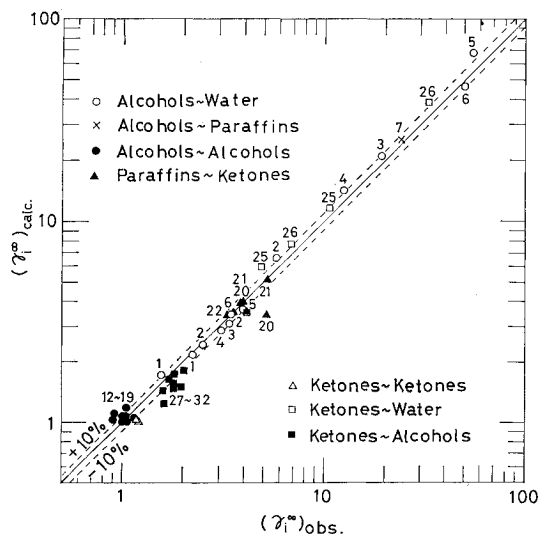Fig. 1 Variation of Group Wilson Parameters with temperature

Fig. 2 Deviations of predicted values from observed infinite dilution binary activity coefficients at 760 mm of Hg

example of such prediction by the application of the ASOG model. First the observed data necessary for determining the group Wilson parameters were predicted by the ASOG model. The absolute arithmetic mean deviation between observed and predicted infinite dilution activity coefficients is 15% for the 6 binary systems as shown in Table 1.

Fig. 2 shows that the predicted infinite dilution binary activity coefficients calculated by Eqs. (3) to

Table 3 Deviations of predicted values from observed vapor-liquid equilibria for binary systems (760 mm of Hg)

No.	System Component (1)	Component (2)	No. of data points	$y_1 \times 1000$ This work	$y_1 \times 1000$ by Derr and Deal's parameters	t [°C] This work	Ref.
	Type CH_2+OH						
1*	Methanol	Water	32	9	12	0.21	30
2*	Ethanol	Water	19	10	23	0.37	23
3*	n-Propanol	Water	16	11	38	0.52	28
4*	i-Propanol	Water[a]	24	20	—	1.03	42
5*	n-Butanol	Water	19	29	40	1.12	31
6	i-Butanol	Water[b]	14	20	—	0.72	12
7	n-Hexane	Ethanol	16	22	17	1.61	38
8	n-Hexane	n-Propanol	12	35	36	1.28	33
9*	Methanol	n-Heptane	7	8	9	0.47	7
10	n-Heptane	n-Propanol	9	17	17	0.82	15
11	n-Heptane	n-Butanol	8	13	18	0.73	2
12*	Methanol	Ethanol	12	12	12	0.37	1
13*	Methanol	n-Propanol	7	24	24	0.31	29
14	Methanol	i-Propanol[a]	8	16	—	1.08	6
15	Methanol	n-Butanol	9	30	30	5.44	19
16*	Ethanol	n-Propanol	9	8	18	0.28	29
17*	Ethanol	i-Propanol[a]	13	2	—	0.11	6
18	Ethanol	n-Butanol	9	11	11	0.20	16
19	i-Propanol	n-Propanol[a]	14	5	—	0.17	6
	Type CH_2+CO						
20	n-Pentane	Acetone	11	21	17	3.09	27
21	Acetone	n-Hexane	9	18	18	1.40	27
22	2,3-Dimethyl butane	Acetone[c]	11	11	—	2.11	40
23	Methyl ethyl ketone	n-Heptane	8	5	10	0.21	2
24	Acetone	Methyl ethyl ketone	16	32	39	1.58	4
	Type $CH_2+OH+CO$						
25*	Acetone	Water	48	13	18	0.60	30
26*	Methyl ethyl ketone	Water	16	19	24	0.67	13
27*	Acetone	Methanol	33	7	6	0.78	30
28*	Acetone	Ethanol	13	17	18	1.11	1
29	Acetone	i-Propanol[a]	25	11	—	0.94	10
30	Methanol	Methyl ethyl ketone	12	8	12	0.61	34
31	Ethanol	Methyl ethyl ketone	10	13	7	1.31	3
32	Methyl ethyl ketone	n-Butanol	6	35	37	2.05	2

[a] ν_{ki} for i-Propanol; $\nu_{CH_2}=2.8$ $\nu_{OH}=1$, [b] ν_{ki} for i-Butanol; $\nu_{CH_2}=3.8$ $\nu_{OH}=1$, [c] ν_{ki} for 2,3-Dimethyl butane; $\nu_{CH_2}=5.6$

(7) plotted against observed values on 32 binary systems appearing in Table 3. As for the calculation of ν_{ki} values for i-propanol, i-butanol and 2,3-dimethyl butane, the CH group is treated as 0.8 CH_2 groups. Values of infinite dilution activity coefficients for systems marked * in column 1 of Table 3 are those obtained by the ebulliometer, while those for the other systems are values obtained by extrapolation to zero composition after calculating activity coefficients on the basis of the relation $\gamma_i = \pi y_i / P_i^\circ x_i$ using vapor-liquid equilibria. As Fig. 2 shows, the estimates generally fall within about ±10%. The infinite dilution activity coefficients for systems including water, like alcohols–water and ketones–water, have been predicted with a fair degree of accuracy. A comparison of predicted and observed infinite dilution activity coefficients in the case of alcohols in water is given in Fig. 3, where the values shown comprise the observed values by the authors and Butler et al.[9], and calculated values by the

Pierotti-Deal-Derr and the Balakrishnan-Krishnan-Eduljee equations[5,32].

Prediction of ternary activity coefficients at infinite dilution has been made for each component in ethanol –n-propanol–water, for n-butanol in ethanol–n-butanol–water and for each component in acetone–methanol–water. The results agree well with the observed ones, as is indicated in Figs. 4 to 6.

Prediction of Vapor-Liquid Equilibria

Prediction of vapor-liquid equilibria has been made on the basis of ASOG model for 32 isobaric binary systems as shown in Table 3. Vapor-liquid equilibria are calculated by Eqs. (11), (12),

$$y_i = \gamma_i P_i^\circ x_i / \pi \tag{11}$$

$$\sum_{i=1}^{n} y_i = \sum_{i=1}^{n} \gamma_i P_i^\circ x_i / \pi = 1 \tag{12}$$

in which the activity coefficients are predicted by applying Eqs. (3) to (7). Table 3 shows the absolute
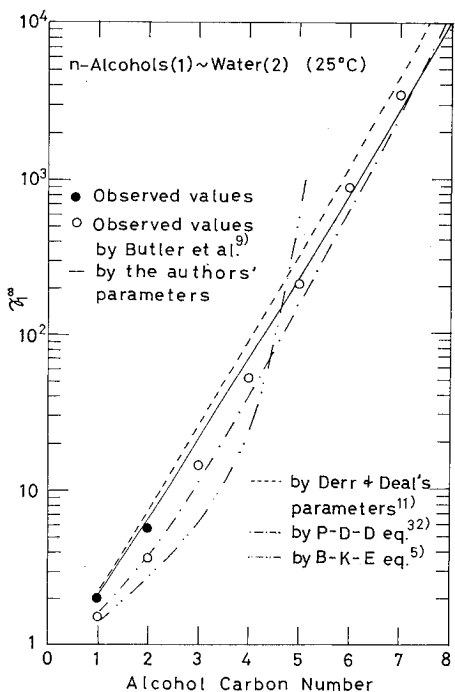
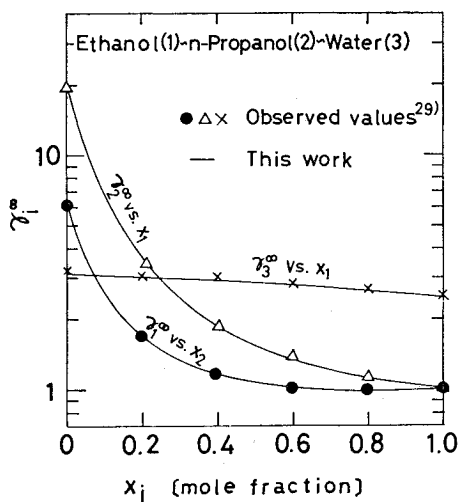Fig. 3 Infinite dilution binary activity coefficients vs. alcohol carbon number

Fig. 4 Infinite dilution ternary activity coefficients vs. concentration at 760 mm of Hg
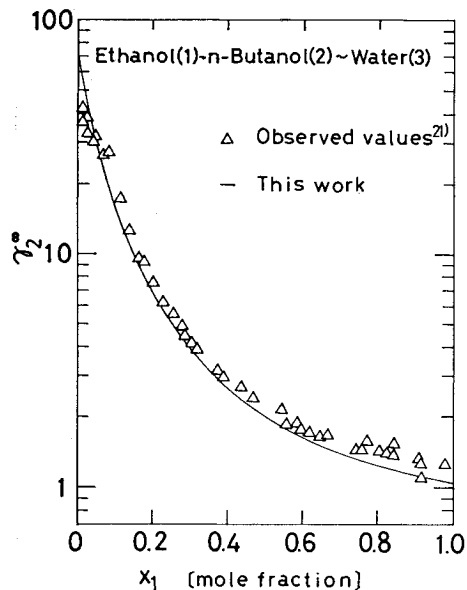

Fig. 5 Infinite dilution ternary activity coefficients vs. concentration at 760 mm of Hg
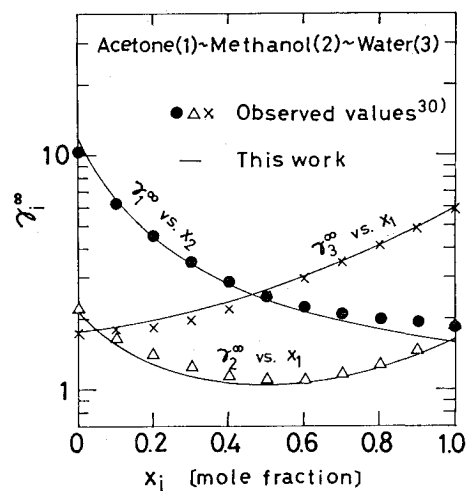

Fig. 6 Infinite dilution ternary activity coefficients vs. concentration at 760 mm of Hg
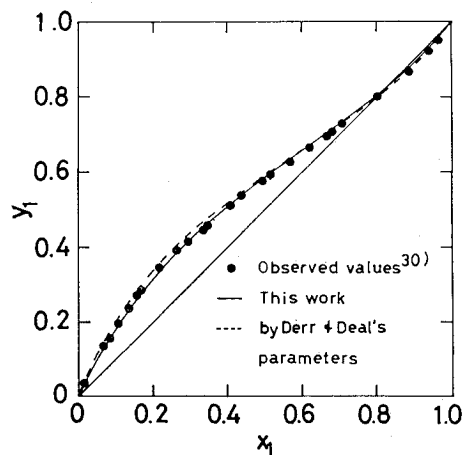
Fig. 7 Vapor-liquid equilibria for Acetone (1)-Methanol (2) at 760 mm of Hg

arithmetic mean deviations between observed and predicted vapor compositions obtained by means of our parameters. In Table 3 the deviations obtained by the parameters of Derr and Deal are also shown. As indicated in Table 3, our parameters give a much better prediction than those of Derr and Deal for the systems including water. For the other systems, too, a similar degree of precision was obtained. The data relating to the 4 systems indicating deviations above 3% did not satisfy the test for thermodynamic consistency proposed by Herington[18]. **Figs. 7** and **8** show comparisons between predicted and observed vapor compositions for acetone-methanol and n-

Table 4 Deviations of predicted values from observed vapor-liquid equilibria for ternary systems (760 mm of Hg)

No.	System Component (1)	Component (2)	Component (3)	No. of data points	Absolute arithmetic deviations in $y_1 \times 1000$	$y_2 \times 1000$	t [°C]	Ref.
	Type CH_2+OH							
1	Methanol	Ethanol	n-Propanol	40	19	9	0.67	20
2	Methanol	n-Propanol	Water	51	17	12	0.36	29
3	Methanol	i-Propanol	Water	56	13	8	0.75	29
4	Ethanol	n-Propanol	Water	54	7	11	0.18	29
5	Ethanol	i-Propanol	Water	53	9	9	0.25	23
	Type $CH_2+OH+CO$							
6	Acetone	Methanol	Water	50	11	8	0.75	30
7	Acetone	Methanol	Ethanol	89	13	12	0.59	1
8	Acetone	Ethanol	n-Hexane	20	14	15	1.73	39
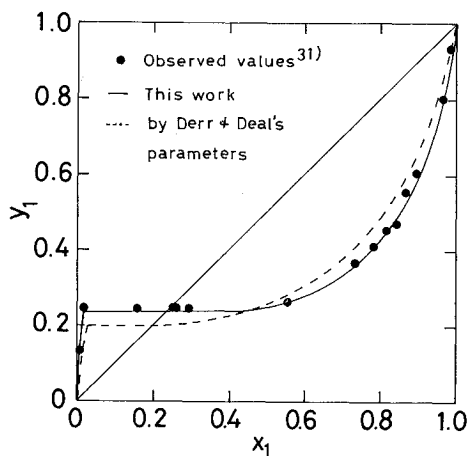
Fig. 8 Vapor-liquid equilibria for n-Butanol (1)–Water (2) at 760 mm of Hg

Observed values[31)]
— This work
···· by Derr + Deal's parameters

butanol–water. Values predicted by means of Derr and Deal's parameters are shown by the dotted lines in Figs. 7 and 8.

Prediction of vapor-liquid equilibria has been made for 8 ternary systems. A comparison of predicted and observed vapor compositions appears in **Table 4** indicating good agreement.

Conclusions

An accurate and rapid method for determining the group Wilson parameters has been developed for predicting liquid phase activity coefficients by the ASOG model applying an ebulliometer. The group Wilson parameters for any system made up of CH_2, OH, CO groups have been determined at 40 to 100°C. Predictions of infinite dilution activity coefficients and isobaric vapor-liquid equilibria made for binary and ternary systems involving alcohols, water, paraffins, ketones showed good agreement with observed values.

Nomenclature

a	= group Wilson parameter	[—]
B, C	= constants of Antoine equation	[—]
P	= vapor pressure	[mmHg]
T	= absolute temperature	[°K]
ΔT	$= T - x_1 T_1 - x_2 T_2$	[°K]
t	= temperature	[°C]

X	= group fraction	[—]
x	= mole fraction in liquid phase	[—]
y	= mole fraction in vapor phase	[—]
Γ	= group activity coefficient	[—]
γ	= activity coefficient	[—]
π	= total pressure	[mmHg]
ν	= number of groups	[—]

⟨Subscripts⟩
$1,2,3,i,j$	= molecule 1, 2, 3, i and j	
k,l,m	= group k, l and m	
ki	= group k in molecule i	

⟨Superscripts⟩
FH	= size contribution	
G	= group contribution	
∞	= infinite dilution	

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ISOBARIC VAPOR-LIQUID EQUILIBRIUM DATA OF PROPIONIC ACID-*m*-XYLENE SYSTEM

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Experimental vapor-liquid equilibrium data have been obtained for the system propionic acid–*m*-xylene at 760 mmHg pressure using a recirculating type equilibrium still. The system formed a minimum boiling azeotrope. The activity coefficients were calculated from experimental data taking into consideration vapor phase imperfection. Nothnagel's correlation based on chemical theory of vapor imperfection was used to estimate second virial coefficients. The data have been tested for thermodynamic consistency and correlated by Wilson equation as modified by Katayama and Tsuboka.

Introduction

With a view to utilize organic acids as entraining agents for the separation of close boiling hydrocarbons, isobaric vapor-liquid equilibrium data for the the system propionic acid–*m*-xylene were obtained at 760 mmHg pressure. This work forms part of a continuing study on vapor-liquid equilibria involving C_8 aromatics and other nonaromatic compounds. No data on this system could be found in the literature. The system formed a minimum boiling azeotrope having a composition of 54.5 mole percent *m*-xylene at 133.75°C. The corresponding azeotropic composition reported by Horsley[5] is 55.1 mole percent *m*-xylene at 132.65°C.

Experimental

Apparatus and procedure

For the analysis of equilibrium mixtures, density and conductometric titration methods were used. The density measurements were made at 25°C with a pycnometer of 3 to 4 m*l* capacity calibrated with conductivity water. The accuracy of the density measurements was of the order of $\pm.0002$ gm/m*l*. In carrying out conductometric titrations N/20 and N/50 sodium hydroxide solutions were used for finding the composition of acid-rich and acid-weak equilibrium mixtures respectively. The accuracy of this method is of the same order as that of the