

## THERMODYNAMICS OF ASSOCIATED SOLUTIONS. VAPOUR–LIQUID EQUILIBRIUM FOR SOLUTIONS CONTAINING PROPANOIC ACID OR BUTANOIC ACID WITH ASSOCIATION IN BOTH PHASES

ISAMU NAGATA

*Department of Chemical Engineering and Division of Physical Sciences, Kanazawa University,  
Kodatsuno 2, Kanazawa 920 (Japan)*

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### ABSTRACT

An association model was developed to correlate the isothermal vapour–liquid equilibrium data of the binary systems propanoic acid + benzene, + *n*-heptane, + chlorobenzene, + cyclohexane, + tetrachloromethane and + 2-butanone, and butanoic acid + 2-butanone. The model uses a concentration-dependent mole fraction association constant for carboxylic acids in the liquid phase, with allowance for molecular interactions between the true chemical species expressed by the NRTL (non-random two liquid) equation. The model quantitatively reproduces the experimental results in a satisfactory manner over the whole composition range.

### LIST OF SYMBOLS

A, B	carboxylic acid and a non-associating component
$a_{ij}$	NRTL binary interaction parameter related to $\tau_{ij}$
$B_{ij}^D$	dimerization contribution to the second virial coefficient for <i>i</i> – <i>j</i> interaction
$B_{ij}^F$	free contribution to the second virial coefficient for <i>i</i> – <i>j</i> interaction
$F$	objective function as defined by eqn. (15)
$f$	fugacity
$G_{ij}$	coefficient as defined by $\exp(-\alpha_{ij}\tau_{ij})$
$K$	liquid-phase thermodynamic association constant for carboxylic acid
$K_x$	liquid-phase mole fraction association constant as defined by $x_{A_2}/x_{A_1}^2$
$K_{ij}^\gamma$	activity coefficient ratio as defined by $\gamma_{A_2}/\gamma_{A_1}^2$
$K_{ij}^V$	vapour-phase equilibrium dimerization constant for <i>i</i> – <i>j</i> pair
$P$	total pressure
$P_i^s$	saturated vapour pressure of pure component <i>i</i>
$R$	universal gas constant

$T$	absolute temperature
$v_i^L$	molar liquid volume of pure component $i$
$x_i$	liquid-phase mole fraction of component $i$ or molecular species $i$
$y_i$	apparent vapour-phase mole fraction of component $i$
$z_i$	true vapour-phase mole fraction of molecular species $i$ at equilibrium

### Greek letters

$\alpha_{ij}$	NRTL non-randomness parameter for $i$ - $j$ pair
$\gamma_i$	activity coefficient of component $i$ or molecular species $i$
$\delta_{ij}$	Kronecker $\delta$ , $\delta_{ij} = 0$ for $i \neq j$ and $\delta_{ij} = 1$ for $i = j$
$\sigma_P, \sigma_T$	standard deviations in pressure and temperature
$\sigma_x, \sigma_y$	standard deviations in liquid-phase and vapour-phase mole fractions
$\tau_{ij}$	NRTL binary parameter as defined by $a_{ij}/T$
$\phi_i$	vapour-phase fugacity coefficient of component $i$ at $T$ and $P$
$\phi_i^s$	vapour-phase fugacity coefficient of pure component $i$ at $T$ and $P_i^s$
$\phi_i^0$	vapour-phase fugacity coefficient of true molecular species $i$

### Subscripts

$A_1, A_2$	monomer and dimer of carboxylic acid
$B_1$	monomer of non-associating component
$i, j, k, l$	chemical molecular species or components

### Superscripts

$\wedge$	calculated value
*	pure-liquid reference state

## INTRODUCTION

Vapour mixtures containing one or more carboxylic acids deviate considerably from ideality, mainly because of strong dimerization between carboxylic acid molecules, although the pressure is far below atmospheric. The fugacity coefficients of the components involved are modelled using the chemical theory of vapour-phase imperfection [1]. In the liquid phase, carboxylic acids partly associate to form dimers. The dimerization constant in the vapour phase is independent of composition and is assumed to be the value of the association constant for the pure associating component. This is not the case for the liquid phase. The liquid-phase mole fraction dimeri-

zation constant in a mixture is not equal to that of the pure associating component and is concentration dependent. The concentration dependence of the dimerization constant appears to make the liquid-phase non-ideality modelling more complex. In previous papers [2,3], an association model was proposed to correlate the isothermal vapour-liquid equilibrium data of binary solutions of acetic acid with benzene, *n*-heptane, toluene, tetrachloromethane, water and 2-butanone and to predict the ternary isothermal vapour-liquid equilibria of acetic acid + toluene + *n*-heptane without any ternary parameters. The new model uses the thermodynamic association constant, which includes a liquid-phase mole fraction association constant for pure acetic acid, to generate a concentration-dependent mole fraction association constant for acetic acid in the mixture. The activity coefficients of true chemical species were expressed by the NRTL (non-random two liquid) equation [4].

Because the new model was not applied to other carboxylic acid-containing solutions, this paper presents the calculated results of vapour-liquid equilibrium data reduction for binary mixtures including either propanoic acid or butanoic acid.

#### SOLUTION MODEL

In a mixture of a carboxylic acid and one non-solvating component, three chemical species  $A_1$ ,  $A_2$  and  $B_1$  exist because of dimerization of the carboxylic acid ( $A_1 + A_1 = A_2$ ). The thermodynamic equilibrium constant of the reaction is defined as

$$K = \frac{x_{A_2}^* \gamma_{A_2}^*}{(x_{A_1}^* \gamma_{A_1}^*)^2} = \frac{x_{A_2} \gamma_{A_2}}{(x_{A_1} \gamma_{A_1})^2} = K_x K_\gamma \quad (1)$$

where  $x_i$  and  $\gamma_i$  are the true mole fraction and true activity coefficient of species  $i$  respectively. The liquid-phase mole fraction dimerization constant  $K_x$  is given by  $x_{A_2}/x_{A_1}^2$  and the activity coefficient ratio  $K_\gamma$  by  $\gamma_{A_2}/\gamma_{A_1}^2$ , and the symbol \* denotes the pure state of the acid. Molecular interactions between the species are expressed by the NRTL equation

$$\ln \gamma_i = \frac{\sum_j \tau_{ji} G_{ji} x_j}{\sum_k G_{ki} x_k} + \sum_j \frac{x_j G_{ij}}{\sum_k G_{kj} x_k} \left( \tau_{ij} - \frac{\sum_l x_l \tau_{lj} G_{lj}}{\sum_k G_{kj} x_k} \right) \quad (2)$$

where

$$\tau_{ji} = a_{ji}/T, \quad (3)$$

$$G_{ji} = \exp(-\alpha_{ji} \tau_{ji}), \quad (4)$$

$\tau_{ji}$  is a binary parameter related to the energy parameter  $a_{ji}$  and  $\alpha_{ji}$  is a non-randomness parameter. For pure carboxylic acids  $\alpha_{A_1 A_2} = \alpha_{A_2 A_1} = 0.3$  (fixed value), and the monomer-dimer interaction parameter for carboxylic

acid might decrease in magnitude in the order acetic acid > propanoic acid > butanoic acid as the alkyl group attached to the carboxylic acid residue increases in size in the order methyl < ethyl < propyl. One energy parameter  $a_{A_1A_2} = a_{A_2A_1}$  is thus tentatively assigned as follows:  $-100$  K for acetic acid [2,3];  $-80$  K for propanoic acid;  $-60$  K for butanoic acid. A further three adjustable parameters are used in fitting the model to experimental data. For the binary systems where no complex formation takes place it is assumed that  $a_{A_1B_1} = 2a_{A_2B_1}$  and  $a_{B_1A_1} = 2a_{B_1A_2}$ , and the resulting parameters are  $a_{A_1B_1}$ ,  $a_{B_1A_1}$  and  $\alpha_{A_1B_1} = \alpha_{B_1A_1} = \alpha_{A_2B_1} = \alpha_{B_1A_2} = \alpha_{AB}$ .

The fugacity of the nominal associating component should be equal to that of the monomer of the associating component [5]. The apparent activities of both components are thus related to the true activities of the monomers of the components as follows

$$x_A \gamma_A = \frac{x_{A_1} \gamma_{A_1}}{x_{A_1}^* \gamma_{A_1}^*} \quad (5)$$

and

$$x_B \gamma_B = x_{B_1} \gamma_{B_1} \quad (6)$$

The apparent mole fractions of the components are expressed in terms of the true mole fractions of the monomers and the equilibrium constant

$$x_A = \frac{x_{A_1} + 2K_x x_{A_1}^2}{x_{A_1} + 2K_x x_{A_1}^2 + x_{B_1}} \quad (7)$$

$$x_B = \frac{x_{B_1}}{x_{A_1} + 2K_x x_{A_1}^2 + x_{B_1}} \quad (8)$$

The sum of the true mole fractions of all the species present should be unity

$$x_{A_1} + K_x x_{A_1}^2 + x_{B_1} = 1 \quad (9)$$

For a given value of  $K$  and a set of the NRTL parameters, the true mole fractions of the monomers are obtained by simultaneous solution of the chemical equilibrium equation (eqn. (1)) and the mass balance equations (eqns. (7) and (9)).

## CALCULATED RESULTS

Vapour-liquid equilibrium calculations are based on the thermodynamic relation

$$P \phi_i y_i = \gamma_i x_i \phi_i^s P_i^s \exp \left[ \frac{v_i^L (P - P_i^s)}{RT} \right] \quad (10)$$

where  $P$  is the total pressure,  $y_i$  is the nominal vapour-phase mole fraction of component  $i$ ,  $P_i^s$  is the pure-component vapour pressure of component  $i$  taken from the original vapour-liquid equilibrium data set,  $v_i^L$  is the pure-liquid molar volume of component  $i$  estimated from the modified Rackett equation [6] and the vapour phase fugacity coefficients,  $\phi_i$  at  $P$  and  $T$  and  $\phi_i^s$  at  $P_i^s$  and  $T$ , are calculated from chemical theory [1].

According to chemical theory, postulating that one or more strongly associating components present in the vapour phase form chemical species, a chemical equilibrium constant for a dimerization equilibrium ( $i + j = ij$ ) is defined by

$$K_{ij}^V = \frac{f_{ij}}{f_i f_j} = \frac{z_{ij}}{z_i z_j} \frac{\phi_{ij}^0}{\phi_i^0 \phi_j^0 P} \quad (11)$$

where  $f$  is the fugacity,  $z$  is the true mole fraction of the chemical species and  $\phi^0$  is the fugacity coefficient of the true species. The chemical equilibrium constant  $K_{ij}^V$  is evaluated using eqn. (12)

$$K_{ij}^V = \frac{-B_{ij}^D(2 - \delta_{ij})}{RT} \quad (12)$$

where  $\delta_{ij} = 0$  for  $i \neq j$ ,  $\delta_{ij} = 1$  for  $i = j$  and  $B_{ij}^D$  is the dimerization contribution to the second virial coefficient [7].

The true fugacity coefficient  $\phi_i^0$  is expressed using the Lewis fugacity rule

$$\ln \phi_i^0 = \frac{B_{ii}^F P}{RT} \quad (13)$$

where  $B_{ii}^F$  is the free contribution to the second virial coefficient [7].  $\phi_{A_1}^0$  is assumed to be equal to  $\phi_{A_2}^0$ .

The calculation of the true mole fraction  $z_i$  is performed by simultaneous solution of mass balance equations for all species and chemical equilibrium equations for all dimerization reactions involved, as shown in detail by Prausnitz et al. [8].

Once the true mole fractions are known, the fugacity coefficient of component  $i$  is calculated from

$$\phi_i = \frac{z_i \phi_i^0}{y_i} = \frac{z_i}{y_i} \exp\left(\frac{B_{ii}^F P}{RT}\right) \quad (14)$$

The computer program used in parameter estimation, based on the maximum likelihood principle, is similar to that described by Prausnitz et al. [8]. Optimum parameters were found by minimizing the objective function

$$F = \sum_i^N \left[ \frac{(P - \hat{P}_i)^2}{\sigma_p^2} + \frac{(T - \hat{T}_i)^2}{\sigma_T^2} + \frac{(x_{1i} - \hat{x}_{1i})^2}{\sigma_x^2} + \frac{(y_{1i} - \hat{y}_{1i})^2}{\sigma_y^2} \right] \quad (15)$$

where a circumflex denotes a calculated value. Standard deviations for

TABLE 1  
Calculated results for binary systems without solvation

System (A + B)	Temp. (°C)	Number of data points	Root-mean-square deviations				Parameters		Variance of fit <sup>a</sup>	Ref.	
			$\delta P$ (Torr)	$\delta T$ (K)	$\delta x$ ( $\times 10^3$ )	$\delta y$ ( $\times 10^3$ )	$a_{A,B}$ (K)	$a_{B,A}$ (K)			$\alpha_{AB}$
Propanoic acid + benzene	40	18 <sup>b</sup>	2.24	0.00	0.0	4.2	-374.47	6246.40	0.3473	8.41	10
Propanoic acid + cyclohexane	25	16	0.61	0.00	0.2		441.93	717.26	0.7842	0.51	11
	45	16	1.17	0.00	0.6		437.90	706.95	0.8221	2.12	11
Propanoic acid + <i>n</i> -heptane	25	14	0.52	0.00	0.0		465.38	705.92	0.5460	0.35	11
	45	14	0.51	0.00	0.0		203.64	615.25	0.0062	0.33	11
	50	16 <sup>c</sup>	0.44	0.00	0.0	6.6	310.93	528.93	0.4892	6.25	12
Propanoic acid + chlorobenzene	40	19	0.26	0.00	0.0	7.4	-561.71	923.15	0.2723	7.39	13
Propanoic acid + 2-butanone	70	10	2.34	0.00	1.0	3.7	-1450.71	2258.37	0.1896	11.36	14
	79	10	2.26	0.00	1.0	2.9	-1289.48	2016.19	0.2252	10.10	14
Propanoic acid + tetrachloro- methane	30	7 <sup>c</sup>	1.67	0.00	0.2	6.3	-963.57	1710.75	0.1573	12.71	15
Butanoic acid + 2-butanone	70	9	1.10	0.00	0.7	2.3	-784.66	1055.50	0.4654	3.52	14
	79	10	1.28	0.00	1.6	6.7	-410.00	39.93	0.9563	12.97	14

<sup>a</sup> Variance of fit = (sum of squared, weighted residuals)/(number of degrees of freedom) =  $F$ /(number of data points - number of parameters).

<sup>b</sup> One erroneous point rejected.

<sup>c</sup> Two erroneous points rejected.

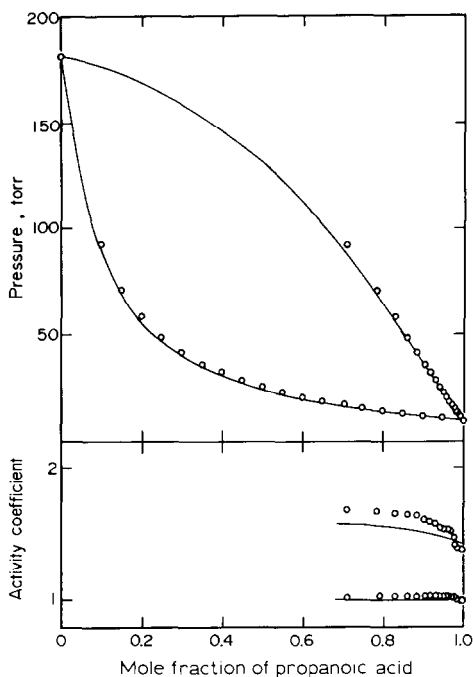


Fig. 1. Vapour-liquid equilibria for propanoic acid + benzene at 40 °C.  $\circ$ , Experimental data of Kogan et al. [10]; —, calculated values.

measured variables were taken to be as follows: pressure,  $\sigma_p = 1$  Torr; temperature,  $\sigma_T = 0.05$  K; liquid mole fraction,  $\sigma_x = 0.001$ ; vapour mole fraction,  $\sigma_y = 0.003$ .

The temperature dependence of the liquid-phase mole fraction dimerization constant for pure carboxylic acids is given by Barton and Hsu [9]. For propanoic acid

$$\ln K_x = \frac{4930}{T} - 8.6632 \quad (16)$$

and for butanoic acid

$$\ln K_x = \frac{5294}{T} - 9.7057 \quad (17)$$

Table 1 gives calculated results for binary systems. Figures 1–7 show comparisons between the calculated results and the experimental values. The variation of the liquid-phase mole fraction dimerization constant as a function of composition is appreciably dependent on each particular system, as shown in Figs. 8–11.

In conclusion, the present association model reproduces the isothermal vapour-liquid equilibria of binary systems of propanoic acid or butanoic

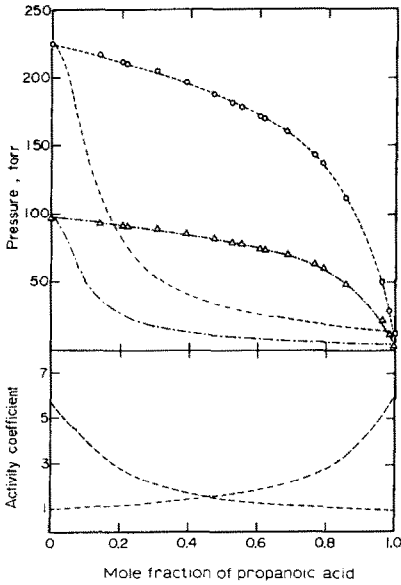


Fig. 2. Vapour-liquid equilibria for propanoic acid + cyclohexane. Experimental data of Lark and Banipal [11]:  $\Delta$ , at 25°C;  $\circ$ , at 45°C. Calculated values: - · - · - ·, at 25°C; - - - - -, at 45°C.

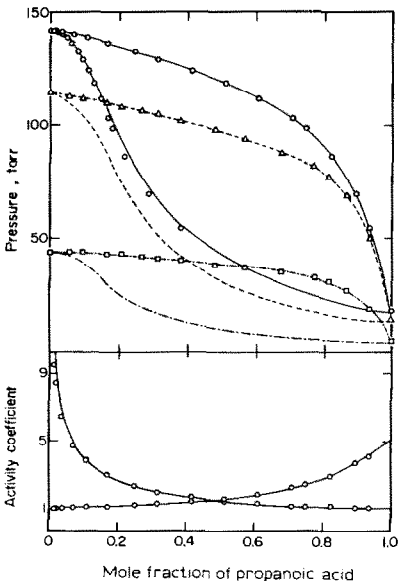


Fig. 3. Vapour-liquid equilibria for propanoic acid + *n*-heptane. Experimental data of Lark and Banipal [11]:  $\square$ , at 25°C;  $\Delta$ , at 45°C.  $\circ$ , Data of Schuberth [12] at 50°C. Calculated values: - · - · - ·, at 25°C; - - - - -, at 45°C; —, at 50°C.



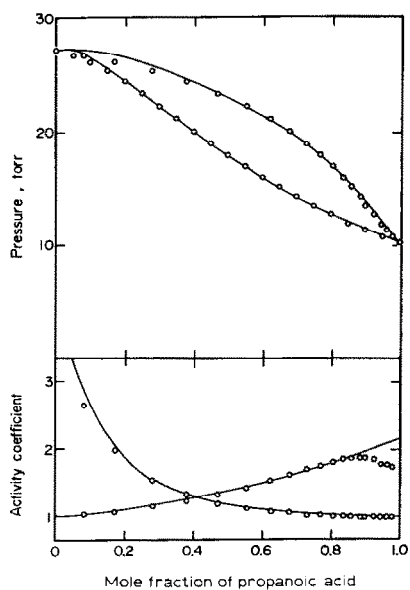


Fig. 4. Vapour-liquid equilibria for propanoic acid + chlorobenzene at 40 °C.  $\circ$ , Experimental data of Kogan et al. [13]; —, calculated values.

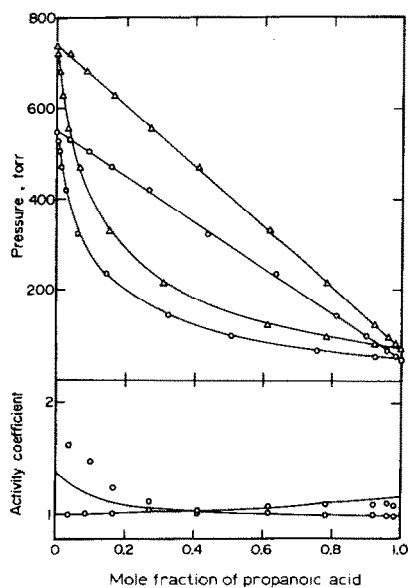


Fig. 5. Vapour-liquid equilibria for propanoic acid + 2-butanone. Experimental data of Rasmussen et al. [14]:  $\circ$ , at 70 °C;  $\Delta$ , at 79 °C. —, Calculated values.

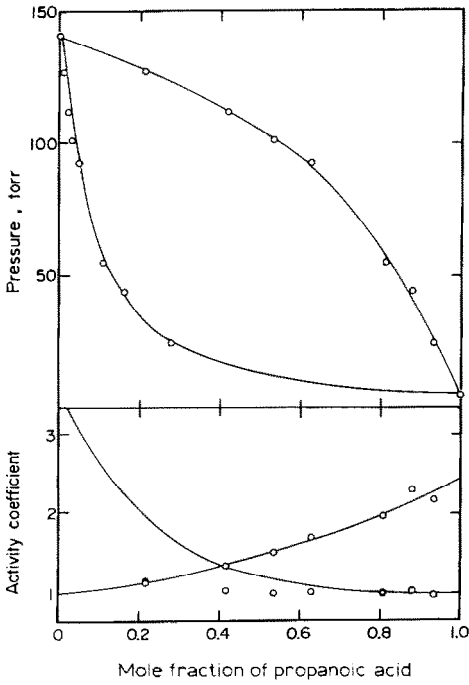


Fig. 6. Vapour-liquid equilibria for propanoic acid + tetrachloromethane at 30°C.  $\circ$ , Experimental data of Tamir et al. [15]; —, calculated values.

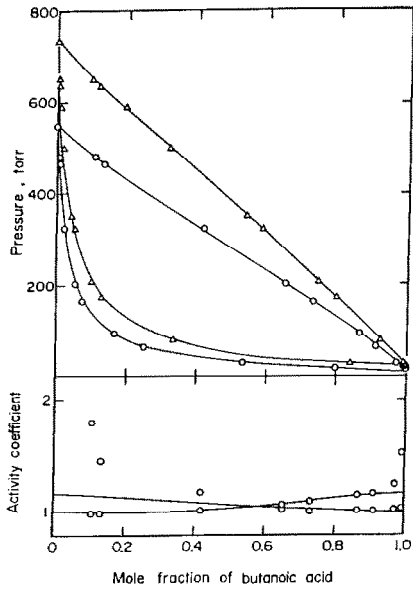


Fig. 7. Vapour-liquid equilibria for butanoic acid + 2-butanone. Experimental data of Rasmussen et al. [14]:  $\circ$ , at 70°C;  $\Delta$ , at 79°C. —, Calculated values.

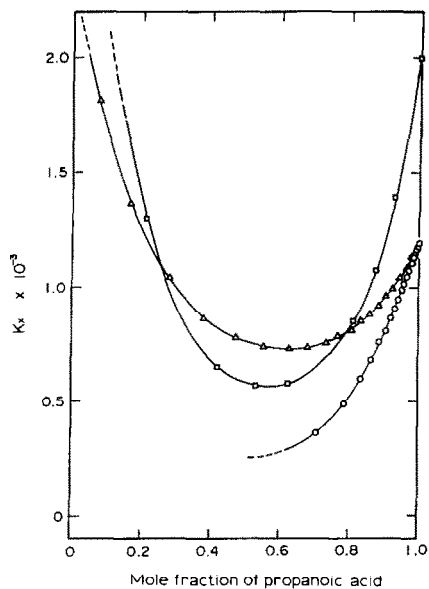


Fig. 8. Variation of liquid-phase mole fraction association constant with composition.  $\circ$ — $\circ$ , Propanoic acid + benzene at 40 °C;  $\Delta$ — $\Delta$ , propanoic acid + chlorobenzene at 40 °C;  $\square$ — $\square$ , propanoic acid + tetrachloromethane at 30 °C.

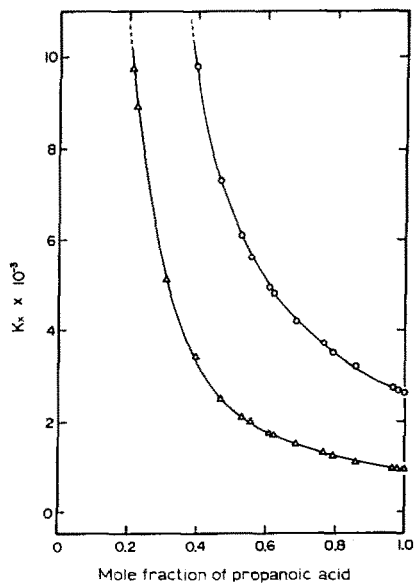


Fig. 9. Variation of liquid-phase mole fraction association constant with composition for propanoic acid + cyclohexane.  $\circ$ — $\circ$ , At 25 °C;  $\Delta$ — $\Delta$ , at 45 °C.

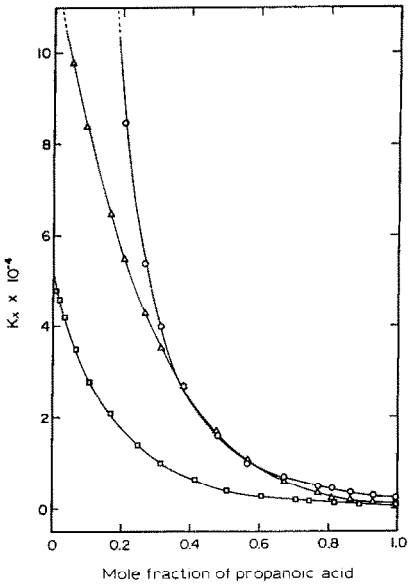


Fig. 10. Variation of liquid-phase mole fraction association constant with composition for propanoic acid + *n*-heptane. ○—○, At 25°C; △—△, at 45°C; □—□, at 50°C.

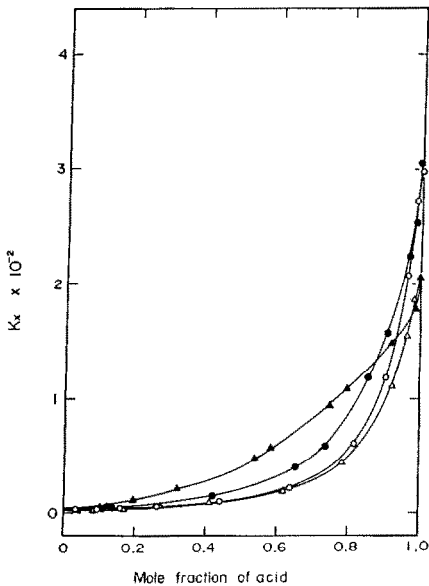


Fig. 11. Variation of liquid-phase mole fraction association constant with composition. Propanoic acid + 2-butanone: ○—○, at 70°C; △—△, at 79°C. Butanoic acid + 2-butanone: ●—●, at 70°C; ▲—▲, at 79°C.

acid with hydrocarbons, chlorobenzene, tetrachloromethane and 2-butanone in a satisfactory manner.

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