CORRELATION OF VAPOR–LIQUID EQUILIBRIA OF ASSOCIATED SOLUTIONS

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An empirical equation is proposed for correlating vapor–liquid equilibrium data of alcohol–hydrocarbon, alcohol–alcohol and alcohol aqueous solutions. It shows a slightly better fitting accuracy than a modified Wilson, NRTL and UNIQUAC equation.

The posibility of correlating pair parameters is also investigated.

Introduction

There is usually a great need for phase–equilibrium data in process design. Several solution theories have been proposed for the correlation of phase–equilibrium relations. However most of them, including the widely used local composition equations, are restricted in the framework of physical molecular interactions. For the highly nonideal solution in which some of its components form associated complexes, these theories are often incapable of expressing the complexity of its excess functions of mixing.

Among those models based on the chemical interaction concept, the associated solution model of Kretschmer and Wiebe[18] and that of Wiehe and Bagley[41] have been successfully applied in representing the excess thermodynamic properties of alcohol–hydrocarbon systems. Both applied the linearly associated solution model to the polymer solution theory of Flory and Huggins,[6,15] although their definition of association constant was different. The Kretschmer–Wiebe model was applied by Renon and Prausnitz[36] to alcohol-saturated hydrocarbon systems and later extended successfully to alcohol-active solvent by Nitta and Katayama.[27] The athermal associated solution model of Wiehe–Bagley was modified by Chen and Bagley[5] with the Scatchard–Hildebrand expression[14] for regular solution as the physical interaction contribution. However, the association constant for specific alcohol was found to be dependent on its solvent. Actually, several authors obtained different values of association constant for each alcohol by data reduction of phase–equilibrium and excess enthalpy data.[25] Moreover, it appears rather difficult to extend both the Kretschmer–Wiebe and Wiehe–Bagley models to those systems containing more than one self-associating component or to alcohol aqueous solutions. Thus their applicability for process design purpose is evidently limited.

Recently, Nath and Bender[25] used the molar enthalpy of vaporization to calculate the enthalpy of association for pure liquids. Thus the association constant can be evaluated from the thermodynamic relation. However, they had to use the UNIQUAC equation[1] for the physical interaction term. As a result, there still remain two adjustable parameters to be determined by VLE data reduction. They also extended their correlation method to the prediction of several ternary systems and revealed the limitation of associated solution theory for extrapolation to multicomponent systems.[26]

Actually there is no precise borderline between chemical and physical effects on the excess thermodynamic properties of associated solutions. The concept of inert solvent may probably be regarded as a matter of convenience. The dividing line between these two effects is essentially only an arbitrary decision.[38] Any effort to separate them would increase the difficulty of computation. From the viewpoint of engineering application, it would be appropriate to combine the chemical and physical effects together into an empirical parameter.

In this paper, an empirical equation is proposed for correlating vapor–liquid equilibrium data of associated solutions. Its applicability has been tested on alcohol aqueous solutions, alcohol–alcohol and alcohol–hydrocarbon systems as well as some systems containing other associating component. The possibility of correlating the pair parameters of various alcohols is also investigated.

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Empirical Equation for Activity Coefficients

Sassa and Katayama[37] have pointed out that the self-association constant of alcohol derived by Wiehe and Bagley[41] is less composition-dependent than that of the Kretschmer–Wiebe equation. However, the Wiehe–Bagley equation takes no account of physical contribution, and as a result the molar volume ratio of alcohol to solvent must be treated as an empirical parameter without any physical significance.[41] Besides, its applicability is limited to alcohol–hydrocarbon systems only. Although Nath and Bender[26] have recently attempted to apply the UNIQUAC associated solution theory to alcohol–alcohol and alcohol aqueous solutions, their prediction accuracies for ternary systems are not as good as those of the Wilson equation.[42]

In fact, the molecular interactions of alcoholic solutions involve self-association and solvation formed by hydrogen bonding, in addition to the physical interaction between monomers and associated complexes. It is impossible to express these three effects by only two adjustable parameters. However, from the viewpoint of engineering application we attempt to combine these effects together into two empirical parameters. This certainly lacks the theoretical rigor of the former theory, but its flexibility of application probably compensates for its loose semitheoretical arguments. From this viewpoint, we try to modify the Wiehe–Bagley equation with the following formulation and test it for the correlation of vapor–liquid equilibrium data of several associated solutions.

For binary systems, the modified Wiehe–Bagley equation can be expressed as follows:

$$\ln\gamma_1=\ln\frac{1+K_{12}}{(1+K_{12})x_1+\rho_{21}x_2}+\frac{1}{K_{12}}\left[\ln(1+K_{12})-\ln\left(1+\frac{K_{12}x_1}{x_1+\rho_{21}x_2}\right)\right]-\frac{\rho_{12}}{K_{21}}\ln\left(1+\frac{K_{21}x_2}{\rho_{12}x_1+x_2}\right) \quad (1)$$

$$\ln\gamma_2=\ln\frac{1+K_{21}}{\rho_{12}x_1+(1+K_{21})x_2}+\frac{1}{K_{21}}\left[\ln(1+K_{21})-\ln\left(1+\frac{K_{21}x_2}{\rho_{12}x_1+x_2}\right)\right]-\frac{\rho_{21}}{K_{12}}\ln\left(1+\frac{K_{12}x_1}{x_1+\rho_{21}x_2}\right) \quad (2)$$

where K_{12} and K_{21} are the two adjustable parameters; x_1 and x_2 are the mole fractions; ρ_{12} and ρ_{21} are the molar volume ratios of component 1 and 2.

For alcohol–alcohol and alcohol aqueous solutions, the binary pair parameters K_{12} and K_{21} contain the contributions of both chemical interaction by hydrogen bonding (self-association and solvation) and the physical interaction among associated complexes. For alcohol–hydrocarbon systems, the pair parameter of hydrocarbon is only of the significance of physical interaction. If we only consider the pair parameter for alcohol and set that of hydrocarbon equal to zero, Eqs. (1) and (2) reduce to the original Wiehe–Bagley equation.[41] (See Appendix)

Data Reduction

A nonlinear least square procedure was applied to obtain the pair parameters of Eqs. (1) and (2) by curve fitting of isobaric and isothermal VLE data. For comparison purposes, three local composition equations (NRTL,[35] UNIQUAC[1] and a modified Wilson equation[39]were also applied to fit the isobaric data.

The modified Wilson equation was proposed by Tsuboka and Katayama.[39] It was tested in our previous paper[43] for twenty binary and three ternary systems. Its superiority over the Wilson equation in correlating and predicting liquid–liquid equilibria was verified.

The fitting accuracies of Eqs. (1) and (2) as well as those of three local composition equations obtained from the isobaric VLE data of 49 binary systems are listed in **Table 1**. Rigorously, we should have considered the temperature dependence of the pair parameters for isobaric data, but since it was only for comparison purposes we neglected this effect in Eqs. (1) and (2). It was found that the proposed equations showed a slightly better fitting accuracy than the three local composition equations.

Correlation of Alcohol Pair Parameters

Although the pair parameters of the proposed equation are in fact of an empirical nature, some possible correlations can be obtained for the pair parameters of various alcohols. For alcohol–hydrocarbon systems, pair parameters of hydrocarbons obtained from VLE data change only slightly with systems and temperatures and are always much smaller than those of alcohols.

Pair parameters for four alcohols obtained from the isobaric VLE data of alcohol–hydrocarbon systems with three different solvents are shown in **Table 2**. The alcohol pair parameters in the alcohol–benzene system are much smaller than those of the same alcohol in saturated hydrocarbons, such as heptane and cyclohexane. If the alcohol pair parameters were plotted against the carbon number of alcohols in logarithmic coordinates, a linear relation was obtained, as shown in **Fig. 1**.

In addition, 81 sets of isothermal VLE data were reduced to investigate the temperature dependence of pair parameters for various alcohols in different solvents. Results are shown in **Table 3**. If the alcohol pair

Table 1. Comparison of fitting accuracies of isobaric VLE data

No.	System	Eqs. (1) & (2)		MW[39]		NRTL[35]		UNIQUAC[1]		Ref.
		ΔY	ΔT	ΔY	ΔT	ΔY	ΔT	ΔY	ΔT	
1	*tert*-Butanol –2-Butanol	1.4	0.4	2.6	0.5	2.3	0.5	2.4	0.5	(44)
2	2-Butanol –1-Butanol	1.0	0.2	1.4	0.2	1.3	0.2	1.3	0.2	(44)
3	*tert*-Butanol –1-Butanol	1.9	0.3	1.8	0.4	1.9	0.4	1.9	0.4	(44)
4	2-Butanol –Isobutanol	0.8	0.2	1.0	0.2	1.1	0.2	1.1	0.2	(44)
5	*tert*-Butanol –Isobutanol	1.3	0.4	1.3	0.4	1.3	0.4	1.2	0.6	(46)
6	Isobutanol –1-Butanol	0.2	0.1	0.2	0.1	0.2	0.1	0.2	0.1	(46)
7	Cyclohexane –2-Butanol	2.1	0.7	2.5	0.7	2.6	0.8	2.7	0.9	(46)
8	Cyclohexane –Isobutanol	2.7	0.1	2.8	0.9	2.8	0.9	2.9	0.8	(47)
9	Cyclohexane –1-Butanol	2.7	0.9	3.7	0.9	3.4	0.8	3.5	1.1	(47)
10	Cyclohexane –*tert*-Butanol	1.7	0.8	1.7	0.7	1.6	0.9	1.8	0.7	(47)
11	Heptane –2-Butanol	1.4	0.7	1.5	0.8	1.5	0.8	1.6	0.7	(47)
12	Heptane –Isobutanol	2.2	0.5	2.1	0.4	2.1	0.3	2.1	0.4	(47)
13	Heptane –1-Butanol	3.1	0.6	3.0	0.5	3.0	0.6	3.0	0.5	(47)
14	*tert*-Butanol –Heptane	0.9	0.7	1.1	0.6	1.1	0.7	1.3	0.6	(47)
15	Cyclohexane –1-Pentanol	3.1	1.8	3.4	1.6	3.2	1.5	3.5	1.3	(47)
16	Methanol –Cyclohexane	1.7	0.7	2.1	0.8	2.0	0.7	3.0	1.9	(23)
17	Methanol –Heptane	0.7	0.5	1.4	0.6	1.3	0.8	1.8	0.9	(4)
18	Ethanol –Methylcyclohexane	1.6	1.1	1.7	0.5	1.6	0.6	1.9	0.8	(16)
19	Hexane –Ethanol	0.7	0.3	1.0	0.3	1.2	0.4	1.9	0.8	(19)
20	Hexane –2-Propanol	0.4	0.1	2.0	0.4	2.1	0.5	2.1	0.6	(10)
21	1-Propanol –Heptane	1.8	0.6	2.5	0.4	2.3	0.5	2.8	0.3	(11)
22	Hexane –1-Hexanol	2.7	1.6	3.5	1.0	3.2	1.0	3.5	1.0	(32)
23	Heptane 1-Hexanol	3.0	1.5	3.9	1.0	3.8	1.2	3.6	0.9	(40)
24	Ethanol –Cyclohexane	1.0	0.4	1.0	0.3	1.5	0.3	1.5	0.3	(24)
25	Ethanol –Hexane	0.9	0.3	0.9	0.2	1.0	0.3	1.7	0.7	(19)
26	Ethanol –1-Butanol	0.8	0.2	1.0	0.8	1.0	0.8	1.0	0.8	(21)
27	Methanol –Ethanol	1.2	0.3	1.2	0.3	1.3	0.3	1.2	0.3	(2)
28	Ethanol –2-Propanol	0.8	0.1	0.8	0.1	0.8	0.1	0.8	0.1	(16)
29	Methanol –2-Propanol	4.2	0.9	4.2	0.9	4.4	0.9	4.2	0.9	(3)
30	Ethanol –Benzene	1.0	0.3	1.0	0.3	1.0	0.2	1.0	0.2	(19)
31	Acetone –Methanol	0.6	0.2	0.6	0.2	0.6	0.2	0.6	0.3	(2)
32	Acetone –Ethanol	2.1	0.6	2.0	0.6	2.0	0.6	2.0	0.6	(2)
33	Ethyl acetate –1-Butanol	2.0	0.6	1.9	0.6	1.9	0.6	1.9	0.6	(12)
34	Methanol –Water	1.0	0.2	0.9	0.2	0.9	0.2	1.0	0.2	(17)
35	Ethanol –Water	1.0	0.5	0.8	0.2	0.9	0.3	0.9	0.3	(16)
36	2-Propanol –Water	1.9	0.7	0.5	0.2	0.5	0.2	0.7	0.3	(16)
37	1-Butanol –Water*	3.4	0.1	2.0	0.6	1.9	0.5	2.3	0.7	(44)
38	*tert*-Butanol –Water	2.5	1.0	2.8	0.3	2.4	0.4	2.2	0.2	(12)
39	2-Butanol –Water*	4.4	1.5	4.5	0.9	4.3	0.9	4.2	1.2	(12)
40	Isobutanol –Water*	3.6	1.3	2.0	0.6	1.9	1.3	1.4	0.8	(44)
41	Water –Isopentanol*	2.7	1.1	4.6	1.4	3.5	1.5	5.1	1.8	(44)
42	Acetoaldehyde–Water	4.2	2.5	4.3	7.1	5.6	3.4	5.1	2.7	(12)
43	Acetone –Water	1.1	0.4	1.4	0.7	0.9	1.1	0.9	0.6	(17)
44	Acetoaldehyde–Ethanol	4.4	1.7	4.4	1.8	4.5	1.8	4.5	1.6	(10)
45	Benzene –2-Propanol	1.5	0.4	1.5	0.3	1.6	0.3	1.6	0.3	(10)
46	Chloroform –Methanol	1.1	0.5	1.2	0.5	1.1	0.6	0.7	0.3	(12)
47	Chloroform –1-Butanol	0.7	0.3	0.8	0.3	0.9	0.5	0.7	0.3	(33)
48	Acetonitrile –2-Butanol	1.1	0.5	1.3	0.4	1.3	0.6	1.2	0.5	(12)
49	Acetonitrile –*tert*-Butanol	1.0	0.4	1.1	0.3	1.1	0.4	1.1	0.4	(12)
	Average deviation =	1.84	0.65	2.04	0.69	1.95	0.67	2.05	0.67	

$$\Delta Y=\sqrt{\sum_{j}^{m}(Y_{j,\mathrm{exp}}-Y_{j,\mathrm{cal}})^2/m}\times 100\,.$$

$$\Delta T=\sqrt{\sum_{j}^{m}\{(t_{j,\mathrm{exp}}-t_{j,\mathrm{cal}})/t_{j,\mathrm{exp}}\}^2/m}\times 100\,.$$

* Systems with limited miscibility.

Table 2. Pair parameters from isobaric VLE data

No.	System (1)	System (2)	Pair parameter K_{12} (alcohol)	Pair parameter K_{21} (hydrocarbon)	Ref.
1	Methanol	–Benzene	27.44	1.36	(8)
			28.75	1.20	(8)
			29.77	1.43	(8)
2	Ethanol	–Benzene	19.03	0.77	(12)
3	1-Propanol	–Benzene	11.44	0.50	(8)
			9.32	1.03	(8)
4	1-Butanol	–Benzene	6.17	0.34	(9)
			7.38	0.19	(9)
5	Methanol	–Heptane	283.86	1.41	(4)
6	Ethanol	–Heptane	44.33	3.58	(8)
			43.82	4.33	(8)
			57.79	4.78	(8)
7	1-Propanol	–Heptane	18.50	1.56	(11)
8	1-Butanol	–Heptane	10.60	2.59	(47)
9	Methanol	–Cyclohexane	449.33	4.76	(23)
10	Ethanol	–Cyclohexane	67.29	2.13	(24)
11	1-Butanol	–Cyclohexane	7.51	2.62	(47)

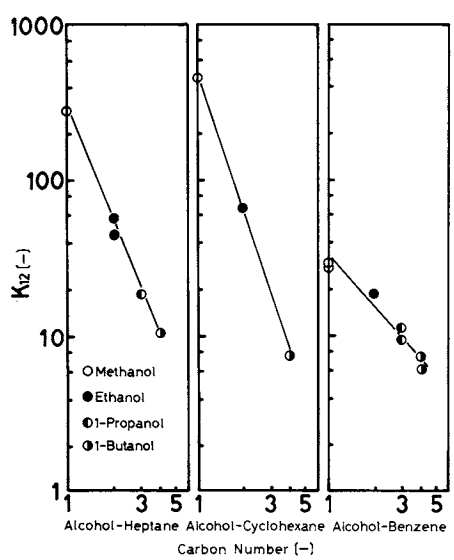

Fig. 1. Alcohol pair parameters vs. carbon number.

parameters were plotted against the reversed absolute temperature on the semi-logarithmic coordinates, linear relations were obtained. For alcohol–benzene systems in **Fig. 2** and alcohol–heptane systems in **Fig. 3**, all lines are nearly parallel and the pair parameters decrease with increasing carbon number of alcohols. However, for alcohol–cyclohexane systems as shown in **Fig. 4**, they are not parallel.

Figure 5 shows the temperature dependence of pair parameters for ethanol in three different solvents. The pair parameter of ethanol changes with solvents. For the ethanol–chloroform system, the pair parameter of chloroform becomes minus. This is probably due to the solvation effect. The temperature dependence of alcohol pair parameters for alcohol aqueous solutions

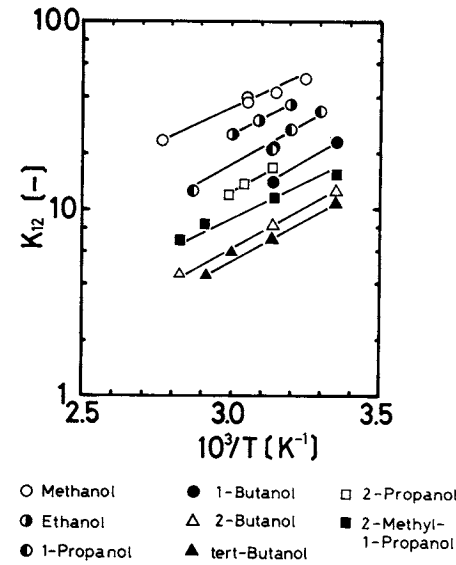

Fig. 2. Temperature dependence of alcohol pair parameters in alcohol–benzene systems.

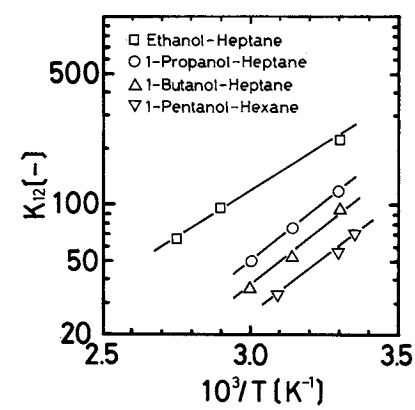

Fig. 3. Temperature dependence of alcohol pair parameters in alcohol–hydrocarbon systems.

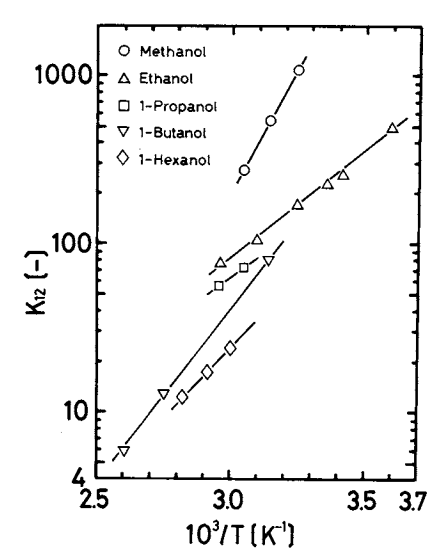

Fig. 4. Temperature dependence of alcohol pair parameters in alcohol–cyclohexane systems.

is also shown in **Fig. 6**.

The values of pair parameters for various alcohols

Table 3. Temperature dependence of pair parameters

No.	System (1)	System (2)	t [°C]	Pair parameter K_{12} (alcohol)	Pair parameter K_{21} (hydrocarbon)	Ref.
1	Methanol	–Benzene	35	49.46	1.32	(8)
				(54.20)		
			45	42.15	1.27	(8)
			55	37.55	1.38	(8)
			55	40.48	1.17	(8)
			90	23.71	0.97	(8)
2	Ethanol	–Benzene	40	36.95	0.86	(8)
			50	30.24	0.89	(8)
				(27.87)*		
			60	25.54	0.81	(8)
3	1-Propanol	–Benzene	30	33.07	0.94	(8)
			40	26.49	0.87	(8)
			45	20.68	0.87	(8)
				(16.30)		
			45	20.81	0.76	(8)
4	2-Propanol	–Benzene	45	16.65	1.68	(9)
				(10.80)		
			55	13.48	0.93	(9)
			60	11.82	1.55	(9)
5	1-Butanol	–Benzene	25	23.09	1.40	(9)
			45	14.11	0.85	(9)
				(12.83)		
6	2-Butanol	–Benzene	25	12.56	1.28	(9)
			45	8.20	1.09	(9)
			80	4.49	0.36	(9)
7	2-Methyl-1-propanol	–Benzene	25	15.16	1.42	(9)
			45	11.54	1.23	(9)
			70	8.35	0.78	(9)
			80	6.81	0.49	(9)
8	*tert*-Butanol	–Benzene	25	10.91	1.50	(9)
			45	7.01	1.36	(9)
			60	5.96	1.27	(9)
			70	4.44	1.16	(9)
9	Ethanol	–Heptane	30	219.28	2.50	(8)
			80	94.60	8.71	(8)
				(46.50)**		
			90	64.67	1.85	(8)
10	1-Propanol	–Heptane	30	111.75	1.13	(8)
				(100.90)		
			45	74.61	1.14	(8)
			60	49.87	1.18	(8)
				(43.63)		
11	2-Propanol	–Heptane	30	95.15	2.84	(8)
				(52.50)		
			45	52.71	2.17	(8)
			60	35.93	1.40	(8)
				(29.50)		
12	1-Pentanol	–Hexane	25	69.39	1.62	(9)
			30	54.67	1.72	(9)
			50	33.56	1.51	(9)
13	Methanol	–Cyclohexane	35	1085.4	5.19	(8)
			45	541.01	5.17	(8)
			55	275.9	7.15	(8)
14	Ethanol	–Cyclohexane	5	490.18	3.12	(8)
				(214.8)		
			20	262.75	2.72	(8)
			25	227.20	2.33	(8)
			35	173.14	2.50	(8)
			50	107.74	2.18	(8)
			65	76.85	1.91	(8)
				(63.36)		

Table 3. (continued)

No.	System (1)	System (2)	t [°C]	Pair parameter K_{12} (alcohol)	Pair parameter K_{21} (hydrocarbon)	Ref.
15	1-Propanol	–Cyclohexane	55	73.37	0.85	(8)
			65	56.73	0.81	(8)
16	1-Butanol	–Cyclohexane	45	80.90	0.64	(9)
			90	12.95	0.32	(9)
			110	5.92	0.53	(9)
17	1-Hexanol	–Cyclohexane	60	24.80	0.39	(9)
			70	17.73	0.38	(9)
			81.2	12.67	0.51	(9)
18	Ethanol	–Methylcyclohexane	0	117.65	10.82	(8)
			35	75.28	5.49	(8)
				(116.0)		
			55	51.36	4.80	(8)
				(76.55)		
19	Ethanol	–Chloroform	35	40.29	−0.66	(8)
			45	33.62	−0.62	(8)
			55	23.74	−0.58	(8)
20	Ethanol	–Toluene	65	9.20	4.87	(8)
				(22.9)***		
			70	9.02	4.70	(8)
			75	8.93	4.40	(8)
			80	8.79	4.47	(8)
			85	8.66	4.42	(8)
21	Methanol	–Water	25	3.50	0.07	(8)
			39.76	3.08	0.07	(8)
			49.76	2.41	0.08	(8)
			50	2.47	0.34	(8)
			62.5	2.29	0.57	(8)
			100	1.17	1.92	(8)
			100	1.14	1.13	(8)
22	Ethanol	–Water	40	8.36	0.97	(8)
			50	7.83	1.68	(8)
			55	7.50	2.28	(8)
			70	7.17	3.27	(8)
			74	6.89	3.78	(8)

Values in parentheses are those calculated by Chen and Bagley.[5]
* At 45°C.
** At 75°C.
*** At 60°C.

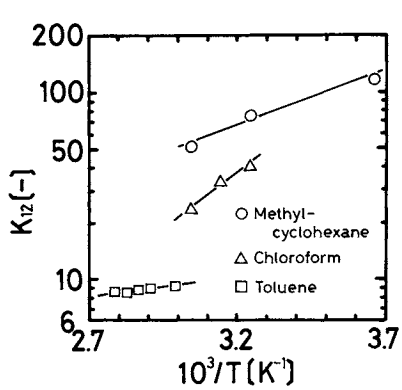

Fig. 5. Temperature dependence of ethanol pair parameters in three solvents.

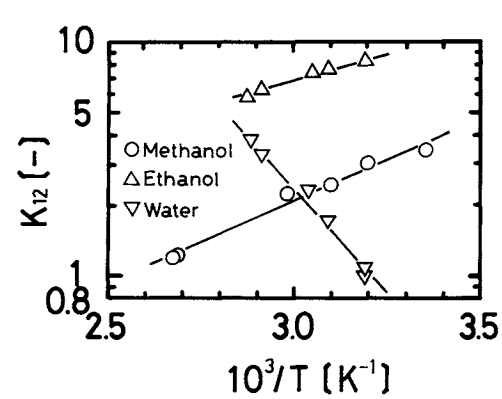

Fig. 6. Temperature dependence of pair parameters in alcohol aqueous solutions.

as given in Table 3 were normalized to 50°C by applying the van't Hoff equation and compared with those obtained by previous investigators as shown in **Table 4**.

From the theoretical standpoint, the association constant of a specific alcohol should remain constant at a fixed temperature in any inert solvent. But the linearly associated solution model is only a simplified

Table 4. Pair parameters of alcohol at 50°C in comparison with association constants suggested by other investigators

Alcohol	Wiehe and Bagley[41]	Renon and Prausnitz[36]	Chen and Bagley[5]	Nath and Bender[25]	Lobien and Prausnitz[22]	This work		
						Benzene	Cyclohexane	Heptane
Methanol	1420	350	25–80	261	50	40	400	—
Ethanol	190	150	27–80	134	40	30	112	150
1-Propanol	—	70	15–153	93	5.6	22	80	65
2-Propanol	—	60	"11	50	—	15	—	—
1-Butanol	55	—	13–28	75	14	14	65	48
2-Butanol	—	—	—	33	—	8	—	—
2-Methyl-1-propanol	—	—	—	48	—	11	—	—
tert-Butanol	—	—	—	16	—	7	—	—
1-Pentanol	—	—	—	—	—	—	—	33
1-Hexanol	—	—	—	58	—	—	35	—

assumption, so it is rather difficult to imagine that the association structure or the degree of association of an alcohol would always remain unchanged in the whole composition range under the influence of physical interaction of various solvents. From this viewpoint, it would be reasonable to assume that the pair parameter of alcohol would also change with different solvent as shown in Fig. 5.

Conclusion

1. The proposed empirical equation is capable of correlating the phase–equilibrium relation of various associated solutions containing more than one associating component with a slightly better fitting accuracy than that of the three local composition equations.
2. In contrast with the energy parameters of local composition equations, the pair parameter of some alcohols obtained from this proposed equation can be correlated with the carbon number of alcohols, and the temperature dependence of pair parameter for various alcohols obeys the van't Hoff rule.
3. Though the association structure of the water molecule is not exactly known, the present equation still appears to be applicable for the correlation of alcohol aqueous solutions.
4. The proposed equation retains the advantage of local composition equations with only two adjustable parameters for each binary system; thus the extension to multicomponent systems is straightforward.

Appendix

Where K_{21} in Eqs. (1) and (2) is approximately equal to zero, by applying the l'Hospital relation,

$$\lim_{K_{21}\to 0}\frac{1}{K_{21}}\ln(1+K_{12})=\lim_{K_{21}\to 0}\frac{1}{1+K_{21}}=1 \tag{3}$$

$$\lim_{K_{21}\to 0}\frac{1}{K_{21}}\ln(1+K_{21}\phi_2)=\lim_{K_{21}\to 0}\frac{\phi_2}{1+K_{21}\phi_2}=\phi_2 \tag{4}$$

By substituting Eqs. (3) and (4) into Eqs. (1) and (2), they can be written as follows:

$$\ln\gamma_1=\ln\frac{1+K_{12}}{(1+K_{12})x_1+\rho_{21}x_2}+\frac{1}{K_{12}}\left[\ln(1+K_{12})-\ln\left(1+\frac{K_{12}x_1}{x_1+\rho_{21}x_2}\right)\right]-\rho_{12}\phi_2 \tag{5}$$

$$\ln\gamma_2=-\ln(\rho_{12}x_1+x_2)+1-\phi_2-\frac{\rho_{21}}{K_{12}}\ln\left(1+\frac{K_{12}x_1}{x_1+\rho_{21}x_2}\right) \tag{6}$$

They are similar to those used by Wiehe and Bagley.[41]

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Nomenclature

K_{12}, K_{21}	=	pair parameter of Eqs. (1) and (2)	[—]
m	=	number of data points	[—]
x_1, x_2	=	mole fraction of components 1 and 2	[—]
γ_1, γ_2	=	activity coefficient of components 1 and 2	[—]
ρ_{ij}	=	molar volume ratio of component i to j	[—]
ϕ_i	=	volume fraction of component i	[—]

Literature Cited

1) Abrams, D. S. and J. M. Prausnitz: *AIChE J.*, **21**, 116 (1975).
2) Amer, H. H. and R. R. Paxton: *Ind. Eng. Chem.*, **48**, 142 (1956).
3) Ballard, L. H. *et al.*: *Ind. Eng. Chem.*, **44**, 245 (1952).
4) Benedict, M., C. A. Johnson, E. Solomon and L. C. Rubbin: *Trans. Am. Inst. Chem. Engrs.*, **41**, 371 (1945).
5) Chen, S. A. and E. B. Bagley: *Chem. Eng. Sci.*, **33**, 153, 161 (1978).
6) Flory, P. J.: *J. Chem. Phys.*, **9**, 660 (1941).
7) Gmehling, J. and U. Onken: "Vapor–Liquid Equilibrium Data Collection," Vol. 1, Part 1, Dechema (1977).
8) Gmehling, J. and U. Onkén: "Vapor–Liquid Equilibrium Data Collection," Vol. 1, Part 2a, Dechema (1977).
9) Gmehling, J., U. Onken and W. Arlt: "Vapor–Liquid Equilibrium Data Collection," Vol. 1, Part 2b, Dechema (1978).
10) Gurukarl, S. M. K. and B. N. Raju: *J. Chem. Eng. Data*, **11**, 501 (1966).
11) "Handbook of Chemistry and Physics," 58th Ed., Chemical Rubber, Cleveland, Ohio (1977–1978).
12) Hirata, M. *et al.*: "Vapor-Liquid Equilibrium Data Book," Kodansha, Tokyo (1975).
13) Harin, S. E.: *Khim. i Khim. Technol.*, **4**, 1564 (1965).

14) Hildebrand, J. H. and R. L. Scott: "Solubility of Non-Electrolytes," Reinhold, New York (1950).
15) Huggins, M. L.: *J. Chem. Phys.*, **9**, 440 (1941).
16) Kojima, K. *et al.*: *Kagaku Kogaku*, **32**, 441 (1968).
17) Kojima, K. *et al.*: *Kagaku Kogaku*, **35**, 584 (1971).
18) Kretschmer, C. B. and R. J. Wiebe: *J. Chem. Phys.*, **22**, 1697 (1954).
19) Kugriavz, L. S.: *Zh. Prikl. Khim.*, **36**, 1471 (1963).
20) Lacmann, R.: *Z. Physik. Chem., Neue Folge*, **23**, 313 (1960).
21) Langley, R. W. and M. M. van Winkle: *Ind. Eng. Chem.*, **45**, 624 (1953).
22) Lobien, G. M. and J. M. Prausnitz: *Fluid Phase Equilibria*, **8**, 149 (1982).
23) Marinichev, A.: *Zh. Prikl. Khim.*, **38**, 1619 (1965).
24) Nagata, I.: *J. Chem. Eng. Data*, **7**, 461 (1962).
25) Nath, A. and E. Bender: *Fluid Phase Equilibria*, **7**, 275, 289 (1981).
26) Nath, A. and E. Bender: *Fluid Phase Equilibria*, **10**, 43 (1983).
27) Nitta, T. and T. Katayama: *J. Chem. Eng. Japan*, **6**, 1 (1973).
28) Nitta, T. and T. Katayama: *J. Chem. Eng. Japan*, **6**, 224 (1973).
29) Nitta, T., J. Itami and T. Katayama: *J. Chem. Eng. Japan*, **6**, 302 (1973).
30) Nitta, T. and T. Katayama: *J. Chem. Eng. Japan*, **7**, 381 (1974).
31) Prigogine, I. and R. Defay: "Chemical Thermodynamics," Longman, London (1954).
32) Rao, B. V. S.: *J. Appl. Chem.*, **18**, 166 (1968).
33) Rao, B. V. S. and C. V. Rao: *Chem. Eng. Sci.*, **17**, 574 (1962).
34) Reid, R. C., J. M. Prausnitz and T. K. Sherwood: "The Properties of Gases and Liquids," 3rd Ed., McGraw-Hill, New York (1977).
35) Renon, H. and J. M. Prausnitz: *AIChE J.*, **14**, 135 (1968).
36) Renon, H. and J. M. Prausnitz: *Chem. Eng. Sci.*, **22**, 299 (1967).
37) Sassa, Y. and T. Katayama: *J. Chem. Eng. Japan*, **6**, 31 (1973).
38) Spala, E. E. and N. L. Ricker: *Ind. Eng. Chem., Process Des. Dev.*, **21**, 409 (1982).
39) Tsuboka, T. and T. Katayama: *J. Chem. Eng. Japan*, **8**, 181 (1975).
40) Vijayaraghavan, S. V. *et al.*: *J. Chem. Eng. Data*, **11**, 147 (1966).
41) Wiehe, I. A. and E. B. Bagley: *Ind. Eng. Chem., Fundamentals*, **6**, 209 (1967).
42) Wilson, G. M.: *J. Am. Chem. Soc.*, **86**, 127 (1964).
43) Zheng, X. Y.: *Bull. Dalian Inst. Tech.*, **17**, 48 (1978).
44) Zong, Z. L. and X. Y. Zheng: *Bull. Dalian Inst. Tech.*, **18**, 18 (1979).
45) Zheng, X. Y. and Z. L. Zong: *Bull. Dalian Inst. Tech.*, **19**, 59 (1980).
46) Zong, Z. L. and X. Y. Zheng: *Bull. Dalian Inst. Tech.*, **19**, 73 (1980).
47) Zong, Z. L. and X. Y. Zheng: *Bull. Dalian Inst. Tech.*, **20**, 63 (1981).

LATERAL SOLID MIXING IN A PACKED FLUIDIZED BED

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Key Words: Mixing, Chemical Reactor, Fluidized Bed, Diffusion Model, Cylindrical Screen Packing, Dispersion Coefficient, Particles Behavior

The lateral mixing of fluidized particles in a packed fluidized bed with cylindrical screen packings was investigated from the unsteady state behavior of tracer particles. The tracer particles were activated alumina particles on which zinc acetate was adsorbed. The lateral mixing characteristics were analyzed by a diffusion model. The lateral dispersion coefficient of the particles was strongly affected by packing size, fluidized gas velocity, and the minimum fluidized gas velocity of the particles. An empirical equation for the lateral dispersion coefficient of the particles in a packed fluidized bed with cylindrical screen packings was obtained.

Introduction

Fluidized beds are used for drying of particles and in solid-gas reactors such as coal combustors, regenerators of spent activated carbon and zinc blende roasters. To analyze these processes it is very important to estimate the residence time distribution of fluidized particles in the bed.

The behaviour of fluidized particles has usually been analyzed by the following models: turnover rate model,[6] diffusion model[2,4,5] and two-phase model.[1] However, the relationship between the model parameters of these models and the operating conditions of the fluidized bed is not established yet.

Generally, mixing of fluidized particles in an ordinary fluidized bed is very fast and to control the mixing rate, suitable internals in the bed are quite effective.

Gabor[3] investigated lateral solid mixing in a packed fluidized bed with sphere packings and analyzed it

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