- (1979).
- 9) *idem*: *Ind. Chem. Eng. Fundam.*, **19**, 219 (1980).
 - 10) Chapman, S. and T. G. Cowling: "Mathematical Theory of Non-Uniform Gases", Cambridge University Press (1951).
 - 11) Fuller, E. N., P. D. Schetler and J. C. Giddings: *Ind. Eng. Chem.*, **58**, 19 (1966).
 - 12) Gilliland, E. R.: *Ind. Eng. Chem.*, **26**, 681 (1934).
 - 13) Gould, R. F., Ed.: "Physical Properties of Chemical Compounds", Am. Chem. Soc. (1959).
 - 14) Lee, C. Y. and C. R. Wilke: *Ind. Eng. Chem.*, **46**, 2381 (1954).
 - 15) Lugg, G. A.: *Anal. Chem.*, **40**, 7, 1072 (1968).
 - 16) Marrero, T. R. and E. A. Mason: *J. Chem. Phys. Ref. Data*, **1**, 1, (1972).
 - 17) Mato, F. and J. L. Bueno: *An. Quim.*, **73**, 108 (1977).
 - 18) Othmer, D. F.: *Ind. Eng. Chem., Anal. Ed.*, **20**, 763 (1948).
 - 19) Perry, R. H. and C. H. Chilton: "Chemical Engineering Handbook", McGraw-Hill, New York (1973).
 - 20) Pommersheim, J. M.: *Ind. Eng. Chem. Fundam.*, **10**, 154 (1971).
 - 21) Reid, R. C. and T. K. Sherwood: "The Properties of Gases and Liquids", McGraw-Hill, New York (1966).
 - 22) Sánchez, V.: Private communication, Laboratoire de Chimie-Physique, Université Paul Sabatier, Toulouse (1977).
 - 23) Seager, S. L., L. R. Geertson and J. C. Giddings: *J. Chem. Eng. Data*, **8**, 168 (1963).
 - 24) Slattery, J. C. and R. B. Bird: *AIChE J.*, **4**, 137 (1958).

AN EQUATION TO CORRELATE BINODAL CURVES IN A TERNARY LIQUID MIXTURE

FUKUJI YAMASHITA, AKIHIRO IGUCHI, SIGEFUMI FUJITA AND HIDEO YOSHII
Department of Chemical Process Engineering, Ikutoku Technical University, Atsugi 243-02

Introduction

Mutual solubility and equilibrium data are required in liquid-liquid extraction. Though many methods of equilibrium data correlation have been previously presented for ternary liquid systems^{1,3,4,9,11}, there are only a few investigations of mutual solubility data correlation^{5,10,12}.

Nam *et al.*¹⁰ have shown that mutual solubility data are correlated by plotting $x_A/(1-x_B)$ against $\log x_B$, but that not all systems obey their method.

Hlavaty⁵ proposed a polynomial equation to correlate mutual solubility data. But it is not easy to use this equation, because it contains many parameters.

In this work two new equations of mutual solubility data correlation are presented and compared with many data of various liquid-liquid systems with one pair of immiscible liquids.

1. New Equations of Mutual Solubility Data Correlation

1.1 The first equation

The following equation was first tested.

$$X_A = \alpha(X_C - d_1)^m(d_2 - X_C)^n \quad (1)$$

where α , m and n are empirical constants to be determined from experimental data. Though α , m and n

can be determined analytically, they have been determined by the least squares method, linearizing Eq. (1). It has become clear that Eq. (1) correlates fairly well the data of systems whose maximum value of X_A is smaller than 0.6, though Eq. (1) does not give the best correlation for any system.

1.2 The second equation

Modifying Eq. (1), the following equation was devised.

$$X_A = (X_C - d_1)^m(d_2 - X_C)^n / [(X_C - d_1)^m + \alpha(d_2 - X_C)^n] \quad (2)$$

Where α , m , n , and p are empirical constants to be determined from data.

From Eq. (2), the following equation was derived.

$$\alpha(d_2 - X_C)^n(X_C - d_1)^{-m} = (d_2 - X_C)^p X_A^{-1} - 1 \quad (2')$$

If p is given, α , m and n can be determined by the least squares method from Eq. (2)' under the following conditions.

$$d_1 < X_C < d_2 \quad (3)$$

$$\alpha > 0, (d_2 - X_C)^p > X_A \quad (4)$$

From Eqs. (3) and (4), it follows that p is smaller than 1.0 or nearly equal to 1.0.

Equation (2) was compared with the experimental data from the literature under the following cases.

CASE 2-a. p is determined by trial and error to give the lowest root mean square deviation

$$\sigma_{\min}$$

CASE 2-b. $p = 1.0$

Received September 17, 1980. Correspondence concerning this article should be addressed to F. Yamashita.

Table 1 Data of the best correlations

No.	No. of system	X_A	System	X_B	Correlation	σ [%]	α [—]	m [—]	n [—]	p [—]	Ref.
1	2	oxalic acid	nitromethane		2-a	3.78	0.731	0.828	-6.384	-5.163	13
2	2855	1-propanol	"		2-a	4.60	0.533	0.790	-0.167	0.746	13
3	2856	2-propanol	"		2-a	1.86	0.755	0.708	-1.161	-0.134	13
4	2894	methanol	phenol		2-a	6.51	0.604	1.147	-2.068	-1.00	13
5	3055	acetic acid	vinyl acetate		2-a	4.12	0.237	1.069	-0.849	0.572	13
6	3065	acetic acid	ethyl ether		2-a	1.91	0.328	0.928	-0.842	0.454	13
7	3070	"	1-pentanol		2-a	7.49	0.176	0.992	-5.414	-2.246	13
8	3083	"	aniline		2-a	4.29	1.374	0.604	-1.712	-0.600	13
9	3087	"	ethylidene		2-a	1.45	1.085	0.545	-1.675	-0.730	13
10	3089	"	4-methyl-2-pentanone		2-a	1.51	0.313	0.972	-1.300	0.154	13
11	3094	acetic acid	2-ethylbutanoic acid		2-a	6.88	0.714	0.723	-3.307	-2.203	13
12	3118	"	2,4-dimethyl-3-pentanol		2-b	2.39	0.908	0.517	3.504	1.0	13
13	3127	"	2-ethylhexanoic acid		2-c	8.26	0.113	1.0	1.724	1.0	13
14	3134	"	glycerol triacetate		2-a	2.92	0.793	0.974	-0.838	0.444	13
15	3227	ethanol	ethyl ether		2-a	3.45	0.484	0.828	-0.976	0.216	13
16	3276	ethanol	benzene		2-a	2.27	0.453	0.639	2.908	1.0066	13
17	3388	"	butoxybutane		2-a	7.42	0.255	0.837	0.287	0.9986	13
18	I-1	acetic acid	<i>n</i> -hexane		2-b	2.94	0.0169	0.680	3.176	1.0	6
19	I-2	"	cyclohexane		2-b	5.68	0.0385	0.444	4.336	1.0	6
20	I-3	"	benzene		2-b	4.21	0.126	0.734	3.010	1.0	7
21	I-4	acetic acid	toluene		2-b	6.81	0.0598	0.846	2.158	1.0	7
22	I-5	"	1,2-dichloroethane		2-a	2.86	0.648	0.450	-8.668	-7.40	2
23	I-6	"	carbon tetrachloride		2-b	4.70	0.0866	0.824	3.394	1.0	6
24	I-7	"	methyl ethyl ketone		2-a	3.80	1.932	0.825	-0.359	0.652	7
25	I-8	"	methyl isobutyl ketone		2-a	4.15	0.297	1.010	-0.973	0.404	7
26	I-9	acetic acid	ethyl acetate		2-a	2.84	0.726	0.866	-0.287	0.628	7
27	I-10	"	<i>n</i> -butyl acetate		2-b	4.41	0.878	0.567	2.385	1.0	7
28	I-11	"	<i>i</i> -amyl acetate		2-a	2.16	0.643	0.637	-12.57	-11.392	7
29	I-12	propionic acid	toluene		2-b	6.11	0.339	0.309	2.687	1.0	8
30	I-13	"	chloroform		2-a	5.82	0.356	0.479	-0.613	0.558	8
31	I-14	propionic acid	carbon tetrachloride		2-a	4.34	0.820	0.231	-6.070	-4.958	8
32	I-15	"	1,2-dichloroethane		2-a	7.50	0.380	0.453	-0.879	0.378	8

Fig. 1 Comparison between experimental solubility data and calculated data by correlation 2-a

Fig. 2 Comparison between experimental solubility data and calculated data by correlation 2-b

CASE 2-c. $p=1.0$, $m=1.0$ CASE 2-d. $p=0.8$ CASE 2-e. $p=0.7$

The root mean square deviation σ is defined by the following equation.

$$\sigma = \left[\frac{1}{S} \sum_{i=1}^S \left| \frac{X_{A,cal,i} - X_{A,exp,i}}{X_{A,exp,i}} \right|^2 \right]^{1/2} \quad (5)$$

2. Results and Discussion

Equation (1) and Eq. (2) with its five cases were compared with experimental data of 32 ternary liquid systems as shown in Table 1, which presents data of

the best correlations.

It has happened that in some cases, Eq. (1) and Eq. (2) give values of X_A much larger than $1 - X_G$ and give an abnormal concavity in plotting X_A against X_G on a triangular graph in a system whose maximum value of X_A is relatively high, even if σ is the lowest. So the conditions of the best correlation require that the correlation does not give X_A much larger than $1 - X_G$ and that it does not give an abnormal concavity.

From Table 1, it is clear that cases 2-a and 2-b give most of the best correlations.

Correlation 2-a gave the best correlation for systems whose maximum value of X_A was smaller than 0.56, and correlation 2-b represented well the data of systems whose maximum value of X_A was between 0.41 and 0.87.

Figures 1 and 2 show examples of the best correlations. These figures and Table 1 show that the correlations of this work are useful.

Nomenclature

d_1	= weight fraction of water in solvent phase at $X_A=0$	[—]
d_2	= weight fraction of water in water phase at $X_A=0$	[—]
i	= integer	[—]
m	= constant	[—]
n	= constant	[—]
p	= constant	[—]
s	= number of data	[—]

X_A	= weight fraction of solute in solution	[—]
$X_{A,cal,i}$	= calculated weight fraction of solute in solution	[—]
$X_{A,exp,i}$	= experimental weight fraction of solute in solution	[—]
X_B	= weight fraction of solvent in solution	[—]
X_G	= weight fraction of diluent(=water) in solution	[—]
α	= constant	[—]
σ	= root mean square deviation defined by Eq. (5)	[—]
σ_{min}	= minimum value of σ	[—]

Literature Cited

- 1) Bechman, I.: *Ind. Eng. Chem. Anal. Ed.*, **12**, 38 (1940).
- 2) Fuse, K. and A. Iguchi: *Kagaku Kōgaku*, **34**, 328 (1970).
- 3) Hand, D. B.: *J. Phys. Chem.*, **34**, 1961 (1930).
- 4) Hirata, M. and S. Fujita: *Kagaku Kōgaku*, **21**, 201 (1957).
- 5) Hlavaty, K.: *Collec. Czech. Chem. Commun.*, **37**, 4005 (1972).
- 6) Iguchi, A. and K. Fuse: *Kagaku Kōgaku*, **34**, 543, 1001, 1226 (1970).
- 7) *idem: ibid.*, **35**, 97, 107, 477, 801 (1971).
- 8) *idem: ibid.*, **36**, 105, 320, 673 (1972).
- 9) Ishida, K.: *J. Chem. Eng. Data*, **6**, 489 (1961).
- 10) Nam, S., T. Hayakawa and S. Fujita: *J. Chem. Eng. Japan*, **5**, 327 (1972).
- 11) Othmer, D. F. and P. E. Tobias: *Ind. Eng. Chem.*, **34**, 693 (1942).
- 12) Salem, A.: *J. Chem. Eng. Japan*, **12**, 236 (1979).
- 13) Stephen, H. and T. Stephen: "Solubility of Inorganic and Organic Compounds", Vol. 2, Pergamon Press (1964).

CORRELATION FOR ACTIVITIES OF WATER IN AQUEOUS ELECTROLYTE SOLUTIONS USING ASOG MODEL

YOSHIHIRO KAWAGUCHI, HITOSHI KANAI, HIROYUKI KAJIWARA AND YASUHIKO ARAI
Department of Chemical Engineering, Kyushu University, Fukuoka 812

The ASOG (Analytical Solutions of Groups) model^{1,7,12)} has successfully been applied to predict phase equilibria^{5,9-11)} using group Wilson parameters. In the present study, the ASOG model is extended to correlate activities of water in aqueous electrolyte solutions.

The activity coefficient of component i in liquid solution is usually given by the ASOG model⁵⁾ as follows.

Received October 20, 1980. Correspondence concerning this article should be addressed to Y. Arai. Y. Kawaguchi is now at Mitsubishi Heavy Ind., Ltd., Tokyo 100, H. Kanai is now at Arabian Oil Company Ltd., Tokyo 100 and H. Kajiwara is now at Sumitomo Chemical Co., Ltd., Osaka 554.

$$\ln \gamma_i = \ln \gamma_i^{FH} + \ln \gamma_i^G \quad (1)$$

where

$$\ln \gamma_i^{FH} = \ln (\nu_i^{FH} / \sum_j x_j \nu_j^{FH}) + 1 - \nu_i^{FH} / \sum_j x_j \nu_j^{FH} \quad (2)$$

$$\ln \gamma_i^G = \sum_k \nu_{ki} (\ln \Gamma_k - \ln \Gamma_k^{(i)}) \quad (3)$$

The activity coefficient for group k , Γ_k , is given by

$$\ln \Gamma_k = -\ln \sum_l X_l a_{l/k} + 1 - \sum_l (X_l a_{l/k} / \sum_m X_m a_{l/m}) \quad (4)$$

where

$$X_k = \sum_i x_i \nu_{ki} / \sum_i x_i \sum_k \nu_{ki} \quad (5)$$

To calculate γ_i at given mole fraction, the group