ington, DC; Israel Program for Scientific Translations, U.S. Department of Commerce, CFSTI: Springfield, VA, 1970).
(11) "Powder Diffraction File"; JCPDS, International Center for Diffraction Data: Swarthmore, PA 19081.
(12) Lee, T. S.; Chiotti, P.; Mason, J. T. *J. Less-Common Met.* **1979**, *66*, 33.
(13) Seward, R. P. *J. Am. Chem. Soc.* **1942**, *64*, 1053.
(14) Seward, R. P. *J. Am. Chem. Soc.* **1955**, *77*, 5507.
(15) Khitrov, V. A. *Izv. Sekt. Fiz.-Khim. Anal., Inst. Obshchei. Neorg. Khim., Akad. Nauk SSSR* **1954**, *25*, 236.

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Isothermal Vapor–Liquid Equilibria for the Ternary Methanol–Ethanol–Benzene System

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Vapor–liquid equilibrium data were measured for the methanol–ethanol–benzene system at 25 °C by using a Boublik vapor–liquid recirculation still. The results are correlated by the UNIQUAC and extended UNIQUAC models with binary parameters estimated from the maximum likelihood method.

In continuation of studies on isothermal vapor–liquid equilibria (VLE) for ternary alcohol mixtures, VLE data for the methanol–ethanol–benzene system at 25 °C are presented, because VLE data for ternary mixtures containing two alcohols are rarely available in the literature and VLE data for all three component binary systems at 25 °C have been published: methanol–ethanol (*1*), methanol–benzene (*2*), ethanol–benzene (*3*).

Experimental Section

All chemicals (first grade) were supplied by Wako Pure Chemical Industries, Ltd., and were purified. Alcohols were fractionally distilled in a 1-m column packed with McMahon packing after drying over drying materials: for methanol, anhydrous copper sulfate; and for ethanol, calcium oxide. Benzene was subjected to repeated recrystallization. Densities, measured with an Anton Paar DMA40 densimeter, and vapor pressures of these compounds at 25 °C are compared with literature values as shown in Table I.

The still used to obtain VLE data for the ternary system was a Boublik vapor–liquid recirculation still (*3*). This still has some advantages as follows: relatively easy operation at 25 °C, high accuracy at low pressure, and no stopcock in contact with sample liquids. Figure 1 shows the all-glass equilibrium still with modifications. An internal platinum heater was inserted into the boiling flask in order to boil the liquid smoothly, and mixing within the liquid sample tubes was performed by magnetic stirrers. A copper–constantan thermocouple calibrated against a Hewlett-Packard 2804A standard quartz thermometer and a Yokogawa P-7B potentiometer connected to a galvanometer were used to measure the equilibrium temperature. The equilibrium pressures were measured by using a mercury manometer and a cathetometer and then corrected to give the equivalent height of a mercury column at 0 °C and standard gravity. The still was loaded with about 80 cm^3 of mixture. The pressure in the still was adjusted until a temperature of 25 °C in the equilibrium was maintained. Liquid samples of two phases in equilibrium were obtained when each experimental run had continued at 25 °C for 2–3 h.

The compositions of the obtained liquid and condensated vapor samples were determined by using a Shimadzu GC-7A gas chromatograph equiped with a Shimadzu ITG-2A digital integrator. The observed values were estimated to have the following experimental errors: pressure, 13 Pa; composition, 0.002 mole fraction; temperature, 0.05 K.

Table I. Densities and Vapor Pressures of Components at 25 °C

	density, g cm^{-3}		vapor press., kPa	
compd	this work	lit. (*4*)	this work	lit. (*4*)
methanol	0.7866	0.786 64	16.692	16.669
ethanol	0.7850	0.785 04	7.973	7.969
benzene	0.8737	0.873 70	12.772	12.692

Experimental Results and Correlations

Experimental vapor–liquid equilibrium data are given in Table II with values of activity coefficients calculated from the relation

$$\gamma_i = \phi_i y_i P / \{\phi_i^s x_i P_i^s \exp[v_i^L (P - P_i^s)/RT]\} \tag{1}$$

where the fugacity coefficients, ϕ_i and ϕ_i^s, were calculated by using the volume-explicit virial equation truncated after the second term and second virial coefficients estimated from the Hayden and O'Connell method (*5*). The virial coefficients are reported in Table II. The liquid molar volumes v_i^L were calculated from the modified Rackett equation (*6*).

The ternary VLE data were correlated with the UNIQUAC and extended UNIQUAC activity coefficient models (*7*, *8*). The UNIQUAC model gives the activity coefficient for any component *i* in a multicomponent mixture by

$$\ln \gamma_i = \ln (\Phi_i/x_i) + 1 - \Phi_i/x_i - (Z/2)q_i\{\ln (\Phi_i/\theta_i) + 1 - \Phi_i/\theta_i\} - q_i' \ln (\sum_j \theta_j'\tau_{ji}) + q_i' - q_i'\sum_j \frac{\theta_j'\tau_{ij}}{\sum_k \theta_k'\tau_{kj}} \tag{2}$$

where *Z* is the coordination number equal to 10, and the segment fraction Φ, the area fractions θ and θ', and an adjustable parameter τ_{ij} are given by

$$\Phi_i = r_i x_i / \sum_j r_j x_j \tag{3}$$

$$\theta_i = q_i x_i / \sum_j q_j x_j \tag{4}$$

$$\theta_i' = q_i' x_i / \sum_j q_j' x_j \tag{5}$$

$$\tau_{ij} = \exp(-a_{ij}/T) \tag{6}$$

The pure-component structural parameters for each component are as follows: for methanol, $r = 1.43$, $q = 1.43$, $q' = 0.96$; for ethanol, $r = 2.11$, $q = 1.97$, $q' = 0.92$; and for benzene,

Table II. Experimental Vapor-Liquid Equilibrium Data for the Methanol (1)-Ethanol (2)-Benzene (3) System at 25 °C[a]

point	x_1	x_2	x_3	y_1	y_2	y_3	P, kPa	γ_1	γ_2	γ_3	ϕ_1	ϕ_2	ϕ_3
1	0.089	0.229	0.682	0.176	0.202	0.622	18.918	2.259	2.084	1.350	0.989	0.989	0.991
2	0.269	0.065	0.666	0.439	0.045	0.516	22.531	2.206	1.936	1.367	0.983	0.983	0.993
3	0.464	0.073	0.463	0.487	0.040	0.473	23.905	1.502	1.622	1.915	0.980	0.981	0.994
4	0.682	0.089	0.229	0.569	0.032	0.399	22.878	1.141	1.018	3.134	0.979	0.981	0.997
5	0.544	0.136	0.320	0.499	0.059	0.442	22.411	1.231	1.205	2.430	0.981	0.982	0.995
6	0.326	0.143	0.531	0.398	0.085	0.517	22.105	1.620	1.632	1.686	0.983	0.984	0.993
7	0.106	0.131	0.763	0.267	0.137	0.596	19.945	3.029	2.600	1.219	0.988	0.987	0.992
8	0.132	0.351	0.517	0.189	0.221	0.590	19.425	1.678	1.526	1.734	0.988	0.988	0.992
9	0.267	0.269	0.464	0.319	0.151	0.530	21.012	1.509	1.467	1.879	0.985	0.985	0.993
10	0.303	0.337	0.360	0.329	0.159	0.512	19.705	1.287	1.157	2.196	0.985	0.986	0.994
11	0.359	0.333	0.308	0.365	0.148	0.487	20.745	1.267	1.146	2.572	0.984	0.984	0.994
12	0.533	0.365	0.102	0.527	0.163	0.310	18.065	1.071	1.003	4.329	0.982	0.984	0.999
13	0.648	0.291	0.061	0.645	0.131	0.224	17.465	1.042	0.977	5.072	0.982	0.984	1.002
14	0.460	0.475	0.065	0.516	0.247	0.237	15.372	1.036	0.996	4.427	0.984	0.986	1.001
15	0.335	0.573	0.092	0.382	0.299	0.319	15.132	1.038	0.984	4.134	0.986	0.987	0.999
16	0.283	0.487	0.230	0.297	0.237	0.466	17.959	1.134	1.089	2.856	0.986	0.987	0.995
17	0.141	0.555	0.304	0.165	0.288	0.547	17.039	1.203	1.104	2.402	0.989	0.989	0.993
18	0.077	0.475	0.448	0.101	0.289	0.610	17.079	1.354	1.299	1.820	0.990	0.990	0.992
19	0.073	0.699	0.228	0.089	0.385	0.526	15.279	1.125	1.052	2.764	0.990	0.990	0.994
20	0.245	0.695	0.060	0.323	0.422	0.255	13.346	1.060	1.012	4.474	0.987	0.989	1.000
21	0.063	0.874	0.063	0.096	0.619	0.285	11.412	1.050	1.011	4.068	0.989	0.991	0.998
22	0.404	0.216	0.380	0.416	0.096	0.488	21.572	1.333	1.191	2.172	0.983	0.983	0.994
23	0.189	0.466	0.345	0.219	0.235	0.546	18.465	1.290	1.161	2.289	0.987	0.988	0.993
24	0.191	0.234	0.575	0.286	0.149	0.565	20.012	1.805	1.587	1.539	0.987	0.986	0.992

[a] $B_{11} = -2796$ cm^3 mol^{-1}, $B_{22} = -2170$ cm^3 mol^{-1}, $B_{33} = -1514$ cm^3 mol^{-1}, $B_{12} = -2534$ cm^3 mol^{-1}, $B_{13} = -533$ cm^3 mol^{-1}, $B_{23} = -775$ cm^3 mol^{-1}.

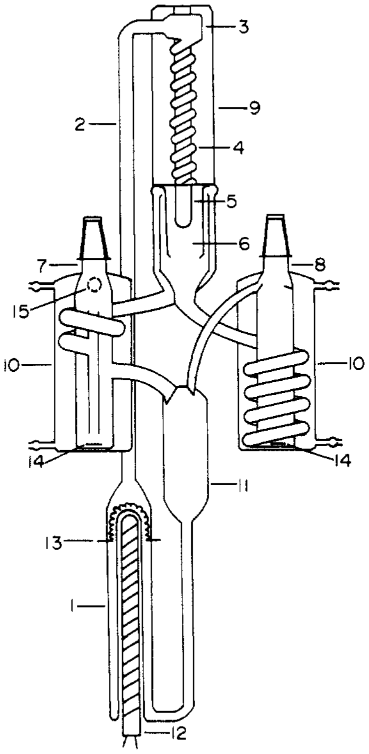

Figure 1. Detailed diagram of Boublik still used: (1) boiling flask, (2) Cottrell pump, (3) expansion chamber, (4) spiral tube, (5) thermometer well, (6) equilibrium chamber, (7) vapor condensate sample tube, (8) liquid sample tube, (9) vacuum jacket, (10) condensers, (11) collector for vapor condensate and liquid samples, (12) external heater, (13) internal platinum heater, (14) magnetic rods, (15) connection to pressure control system.

Table III. Parameters of the UNIQUAC and Extended UNIQUAC Models from Vapor-Liquid Equilibrium Data Correlation at 25 °C

no. of data points	model	rms deviations: ΔP, kPa	rms deviations: ΔT, K	compn, mol %: Δx	compn, mol %: Δy	parameters, K: a_{12}	parameters, K: a_{21}
		Methanol (1)-Ethanol (2)					
11	I[a]	0.1200	0.01	0.02	0.45	-20.72	32.75
	II[b]	0.1093	0.00	0.01	0.40	-39.80	38.88
		Methanol (1)-Benzene (2)					
26	I	0.2093	0.00	0.05		-59.90	1175.16
	II	0.2266	0.00	0.06		63.45	1008.86
		Ethanol (1)-Benzene (2)					
11	I	0.0680	0.00	0.05	0.42	-123.50	1126.79
	II	0.0680	0.00	0.04	0.44	75.30	917.18

[a] I = UNIQUAC. [b] II = extended UNIQUAC.

Table IV. Calculated Results for the Methanol (1)-Ethanol (2)-Benzene (3) System at 25 °C

model	vapor compn, mol %: Δy_1	vapor compn, mol %: Δy_2	vapor compn, mol %: Δy_3	press.: ΔP, kPa	press.: $\Delta P/P$, %
	Mean Deviations				
I[a]	0.62	0.46	0.76	0.2716	1.44
II[b]	0.51	0.49	0.64	0.2570	1.36
	Root-Mean-Square Deviations				
I	0.75	0.58	0.89	0.3184	1.69
II	0.60	0.57	0.78	0.3272	1.72

[a] I = UNIQUAC. [b] II = extended UNIQUAC.

$r = 3.19$, $q = q' = 2.40$. The extended UNIQUAC model for $\ln \gamma_i$ is

$$\ln \gamma_i = \ln (\Phi_i/x_i) + 1 - \Phi_i/x_i - (Z/2)q_i\{\ln (\Phi_i/\theta_i) + 1 - \Phi_i/\theta_i\} - q_i^* \ln (\sum_j \theta_j \tau_{ji}) + q_i \sum_j (q_j^*/q_j)\theta_j - q_i \sum_j \frac{(q_j^*/q_j)\theta_j \tau_{ij}}{\sum_k \theta_k \tau_{kj}} \tag{7}$$

where values of q^* have been empirically obtained for pure components: methanol, 0.99; ethanol, 0.92; benzene, $q^* = q^{0.2}$.

Optimum binary parameters were obtained from the reduction of VLE data for all binary systems which compose the ternary system by using a computer program based on the maximum likelihood principle as described by Prausnitz et al. (*7*). The estimated standard deviations of the measured variables were taken as follows: pressure, $\sigma_P = 0.133$ kPa; temperature, $\sigma_T = 0.05$ °C; liquid mole fraction, $\sigma_x = 0.001$; vapor mole fraction, $\sigma_y = 0.003$. Table III lists the results of the parameter estimation for the two models. These binary pa-

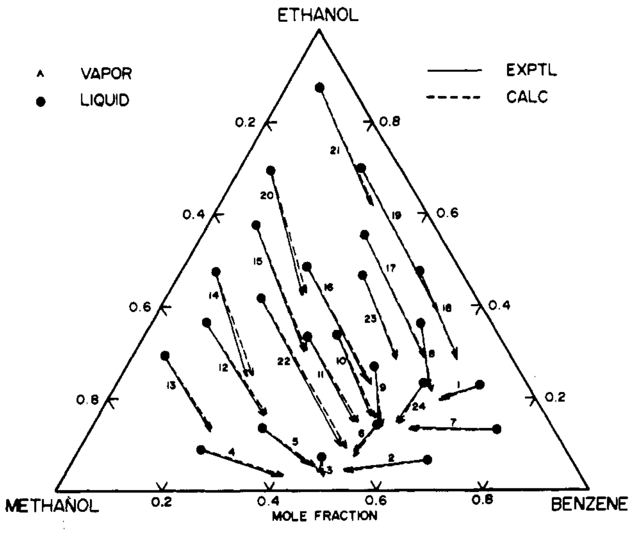

Figure 2. Equilibrium tie lines. Calculated results were obtained from the extended UNIQUAC model.

rameters were used to calculate ternary VLE for the present system without introducing any ternary parameters. Both models gave the errors of the same order of magnitude in the ternary predictions of VLE data as shown in Table IV.

Figure 2 shows the tie lines connecting the liquid and vapor mole fractions in equilibrium, indicating that the system does not involve a ternary azeotrope.

Glossary

a_{ij}	UNIQUAC or extended UNIQUAC binary interaction parameter related to τ_{ij}
P	total pressure
P_i^s	vapor pressure of pure component i
q_i	molecular geometric area parameter for pure component i
q_i'	molecular interaction area parameter for pure component i
q_i^*	correction factor of interaction for pure component i
r_i	molecular volume parameter for pure component i
R	gas constant
T	absolute temperature
v_i^L	molar liquid volume of pure component i
x_i	liquid-phase mole fraction of component i
y_i	vapor-phase mole fraction of component i
Z	lattice coordination number, here equal to 10

Greek Letters

γ_i	activity coefficient of component i
θ_i	area fraction of component i
θ_i'	area fraction of component i in residual contribution to the UNIQUAC activity coefficient
τ_{ij}	UNIQUAC or extended UNIQUAC binary parameter
ϕ_i	fugacity coefficient of component i
ϕ_i^s	fugacity coefficient of pure component i at its saturation pressure
Φ_i	segment fraction of component i

Registry No. Methanol, 67-56-1; ethanol, 64-17-5; benzene, 71-43-2.

Literature Cited

(1) Hall, D. J.; Mash, C. J.; Pemberton, R. C. *NPL Rep. Chem.* (*U.K., Natl. Phys. Lab., Div. Chem. Stand.*) **Jan 1979**, *No. 95*, 1–32.
(2) Hwang, S.-C.; R. L., Jr. *J. Chem. Eng. Data* **1977**, *22*, 319–25.
(3) Ohta, T.; Koyabu, J.; Nagata, I. *Fluid Phase Equilib.* **1981**, *7*, 65–73.
(4) Riddick, J. A.; Bunger, W. B. "Organic Solvents", 3rd ed.; Wiley-Interscience: New York, 1970; pp 107, 145, 147.
(5) Hayden, J. G.; O'Connel, J. P. *Ind. Eng. Chem. Process Des. Dev.* **1975**, *14*, 209–16.
(6) Spencer, C. F.; Danner, R. P. *J. Chem. Eng. Data* **1972**, *17*, 236–41.
(7) Prausnitz, J. M.; Anderson, T. F.; Grens, E. A.; Eckert, C. A.; Hsieh, R.; O'Connell, J. P. "Computer Calculations for Multicomponent Vapor–Liquid and Liquid–Liquid Equilibria"; Prentice-Hall: Englewood Cliffs, NJ, 1980; Chapters 3, 4, 6, Appendices C, D.
(8) Nagata, I. *Thermochim. Acta* **1982**, *56*, 43–57.

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Specific Conductivity of NaCl–AlCl$_3$ and NaCl–AlCl$_3$–Al$_2$S$_3$ Melts

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The specific conductivity of the pure binary NaCl–AlCl$_3$ molten salt system was measured in the temperature range 175–400 °C and with the mole fraction of AlCl$_3$, X_{AlCl_3}, ranging from 0.497 to 0.600. Sulfur, aluminum metal, and sodium chloride were dissolved in the NaCl–AlCl$_3$ solvents at ca. 250 °C, forming polymeric NaAlSCl$_2$. The specific conductivity of these melts was measured in the range $0 < X_{Al_2S_3} < 0.08$. All conductivity data are given as a polynomial function of temperature and composition.

Introduction

It has been shown (*1*) that aluminum metal and elemental sulfur react in alkali tetrachloroaluminate melts in the molar ratio Al:S = 2:3, forming aluminum chlorosulfides. These melts are colorless solutions, possibly containing solute ions like $[Al_nS_{n-1}Cl_{2n+2}]^{n-}$ and $[Al_nS_{n-1}Cl_{2n+2-m}]^{(n-m)-}$ ($n > 3$ and $m > n$). Such melts are of considerable interest as they are formed during discharge of new galvanic cells based on the Al/S couple and the NaAlCl$_4$ electrolyte (*2*, *3*).

The purpose of the present work was to determine analytical expressions for the specific conductivity of NaCl–AlCl$_3$ melts with and without dissolved aluminum chlorosulfides. There are no previous measurements of the conductivity of NaCl–AlCl$_3$ melts containing aluminum chlorosulfides.

Such information is essential in the optimization of the above-mentioned molten salt batteries. Recently we have published (*4*) the liquid densities of the sodium tetrachloroaluminate melts containing aluminum chlorosulfides.

The conductivity of molten NaCl–AlCl$_3$ has previously been studied and a short review is given by Janz et al. (*5*).

For the molten compound NaAlCl$_4$ (50 mol % AlCl$_3$) the equation

$$\kappa = -0.7966 + 2.7366 \times 10^{-3}T \qquad (1)$$

was derived (*5*) from data given by Yamaguti and Sisido (*6*) in the temperature range between 460 and 545 K (187–272 °C). Here, as in the following, the conductivity κ has the units Ω^{-1}

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