the thermodynamic properties of Al_2Cl_6 in pure $AlCl_3$ and in the alkali chloride containing phases in equilibrium with $AlCl_3$. The notable feature is that the enthalpies of vaporization of Al_2Cl_6(gas) are the same within the limits of uncertainty for all three phases at the melting point of $AlCl_3$, while ΔC_p values for the vaporization are nearly equal for the alkali chloride containing phases and less negative than for pure $AlCl_3$(l). This confirms the previous statement (*2*) that the "anomalous" slope of the immiscibility line is most likely attributed to the properties of the $AlCl_3$ phase. That is, $C''_p(Al_2Cl_6)$ in the $AlCl_3$ phase is larger than the partial molar $C'_p(Al_2Cl_6)$ in the ionic mixtures (Table III, last column) due to a greater decrease of attractive forces with temperature in the covalent, near-critical $AlCl_3$ phase. Even though $C'_p(Al_2Cl_6)$ is about equal for the two alkali chloride systems, $C'_p(Al_2Cl_6)$ for the most ionic system, $AlCl_3$–NaCl, as expected deviates the most from that of $AlCl_3$(l) (Table III). The immiscibility gap for the $AlCl_3$–LiCl system (Figure 2) is less than for $AlCl_3$–NaCl, but the variation in immiscibility with temperature is larger for the $AlCl_3$–LiCl system. This is also a simple consequence of a more ideal behavior of the more covalent $AlCl_3$–LiCl mixture.

Safety

Appropriate precautions should be taken for the containment of liquids considerably above their normal boiling points in glass vessels. An especially dangerous situation can occur when $(\rho'' + \rho''')/2 > \rho_{crit}$. The gaseous phase will disappear above a certain temperature and the expansion of liquid $AlCl_3$ will eventually result in rupture of the tube.

Glossary

a	activity of Al_2Cl_6
C_p	heat capacity at constant pressure, J mol^{-1} K^{-1}
H	enthalpy, kJ mol^{-1}
m	mass, g
P	ideal gas pressure of Al_2Cl_6
t, T	temperature, °C and K, respectively
T_M	triple-point temperature of $AlCl_3$, 466.85 K
v	volume, cm^3
X	mole fraction of $AlCl_3$, $AlCl_3$–LiCl scale
y	weight fraction of $AlCl_3$, $AlCl_3$–LiCl scale
ρ	density, g cm^{-3}
0, ′, ″, ‴	superscripts denoting overall sample, $AlCl_3$–LiCl phase, $AlCl_3$(l) phase, and $AlCl_3$(g) phase, respectively

Registry No. $AlCl_3$, 7446-70-0; LiCl, 7447-41-8.

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Received for review February 10, 1982. Accepted August 13, 1982.

Isothermal Vapor–Liquid Equilibria for Six Binary Mixtures

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Isothermal vapor-liquid equilibrium data were reported for six binary systems: ethyl formate–carbon tetrachloride, ethyl formate–chlorobenzene, ethyl formate–toluene, ethyl formate–acetonitrile, chloroform–toluene, and acetonitrile–1-propanol. The experimental data were well correlated with the UNIQUAC equation (Anderson and Prausnitz's modification). The UNIFAC group-interaction parameters were obtained for the groups, ACH/HCOO, $ACCH_2$/HCOO, CCl_4/HCOO, ACCl/HCOO, CCN/HCOO, $ACCH_2/CCl_3$, CCOH/CCN, and OH/CCN.

Introduction

Isothermal vapor–liquid equilibrium data were measured for the following binary systems: ethyl formate–carbon tetrachloride at 318.15 K, ethyl formate–chlorobenzene at 323.15 K, ethyl formate–toluene at 318.15 K, ethyl formate–acetonitrile at 323.15 K, chloroform–toluene at 318.15 K, and acetonitrile–1-propanol at 328.15 K. The experimental results were correlated with Anderson and Prausnitz's UNIQUAC equation (*1*, *12*). The UNIFAC group-interaction parameters for the groups ACH/HCOO, $ACCH_2$/HCOO, CCl_4/HCOO, ACCl/HCOO, CCN/HCOO, $ACCH_2/CCl_3$, CCOH/CCN, and OH/CCN were obtained to extend the range of applicability of the UNIFAC method (*14*).

Table I. Densities and Refractive Indices of Compounds at 298.15 K

compd	density, g/cm³		refractive index	
	exptl	lit.[a]	exptl	lit.[a]
ethyl formate	0.9201[b]		1.359 98[b]	1.359 94[b]
carbon tetrachloride	1.5845	1.584 39	1.457 2	1.457 39
chlorobenzene	1.1010	1.101 12[c]	1.521 7	1.521 9[c]
toluene	0.8622	0.862 31	1.494 1	1.494 13
acetonitrile	0.7767	0.776 6	1.341 6	1.341 63
chloroform	1.4797	1.479 88	1.442 9	1.442 93
1-propanol	0.7995	0.799 75	1.383 5	1.383 70

[a] Reference *13*. [b] At 293.15 K. [c] Reference *16*.

Experimental Procedures

Materials. Guaranteed reagent-grade materials excluding 1-propanol and chloroform were used for experimental work without further purification. Chemically pure grade 1-propanol

Table II. Experimental Isothermal Vapor-Liquid Equilibrium Data for Six Binary Systems

x_1	y_1	P, kPa	γ_1	γ_2	ψ_1	ψ_2
Ethyl Formate (1)-Carbon Tetrachloride (2) at 318.15 K						
0.039	0.145	38.57	1.992	0.992	0.986	0.980
0.133	0.339	46.82	1.651	1.028	0.982	0.976
0.218	0.452	51.37	1.471	1.034	0.980	0.974
0.392	0.598	59.74	1.253	1.130	0.977	0.970
0.424	0.616	60.52	1.209	1.153	0.976	0.970
0.470	0.643	62.09	1.167	1.195	0.976	0.969
0.603	0.728	65.91	1.091	1.288	0.974	0.967
0.668	0.763	67.03	1.049	1.364	0.974	0.967
0.768	0.823	69.42	1.018	1.508	0.973	0.966
0.785	0.835	69.90	1.018	1.528	0.972	0.966
0.835	0.871	70.54	1.007	1.570	0.972	0.966
0.920	0.933	71.74	0.995	1.710	0.972	0.966
Ethyl Formate (1)-Chlorobenzene (2) at 323.15 K						
0.077	0.633	14.53	1.401	1.002	0.994	0.987
0.117	0.727	18.80	1.367	1.004	0.993	0.983
0.318	0.890	36.92	1.201	1.011	0.986	0.967
0.380	0.909	41.94	1.163	1.040	0.984	0.963
0.487	0.934	49.58	1.099	1.070	0.981	0.956
0.546	0.944	54.08	1.079	1.114	0.980	0.952
0.561	0.947	55.34	1.077	1.114	0.979	0.951
0.645	0.959	61.55	1.053	1.179	0.977	0.946
0.659	0.961	62.71	1.051	1.188	0.976	0.945
0.709	0.967	65.57	1.027	1.228	0.975	0.942
0.782	0.975	71.11	1.016	1.340	0.973	0.938
0.889	0.987	78.83	1.000	1.506	0.970	0.931
Ethyl Formate (1)-Toluene (2) at 318.15 K						
0.108	0.559	20.30	1.470	1.007	0.992	0.985
0.298	0.777	34.18	1.239	1.077	0.986	0.974
0.376	0.824	39.41	1.198	1.098	0.984	0.970
0.396	0.834	40.61	1.185	1.101	0.984	0.969
0.516	0.883	47.81	1.130	1.133	0.981	0.964
0.524	0.886	48.30	1.128	1.134	0.981	0.963
0.646	0.922	54.89	1.079	1.179	0.978	0.958
0.844	0.968	65.06	1.023	1.290	0.974	0.950
0.910	0.982	68.21	1.008	1.315	0.973	0.948
Ethyl Formate (1)-Acetonitrile (2) at 323.15 K						
0.038	0.113	36.70	1.280	0.997	0.995	0.945
0.056	0.155	37.98	1.232	1.000	0.994	0.943
0.217	0.446	48.94	1.169	1.004	0.986	0.930
0.372	0.616	57.70	1.104	1.013	0.981	0.921
0.598	0.784	69.25	1.042	1.056	0.975	0.911
0.692	0.838	74.03	1.027	1.100	0.973	0.907
0.765	0.879	76.99	1.011	1.117	0.971	0.905
0.861	0.920	81.97	0.999	1.323	0.969	0.901
Chloroform (1)-Toluene (2) at 318.15 K						
0.160	0.493	16.08	0.871	0.977	0.994	0.988
0.485	0.842	31.32	0.950	0.956	0.988	0.977
0.554	0.875	34.64	0.955	0.963	0.987	0.974
0.588	0.890	36.18	0.955	0.957	0.986	0.973
0.604	0.900	37.54	0.975	0.938	0.986	0.972
0.716	0.940	43.57	0.995	0.907	0.984	0.968
0.946	0.993	55.32	1.005	0.700	0.979	0.959
Acetonitrile (1)-1-Propanol (2) at 328.15 K						
0.048	0.295	21.42	3.329	1.002	0.975	0.988
0.121	0.467	27.58	2.665	1.055	0.966	0.987
0.225	0.581	32.21	2.067	1.097	0.959	0.986
0.349	0.655	35.85	1.662	1.197	0.953	0.986
0.422	0.682	37.32	1.486	1.293	0.951	0.986
0.528	0.719	38.77	1.298	1.455	0.949	0.987
0.659	0.769	40.14	1.149	1.715	0.947	0.987
0.730	0.797	41.37	1.106	1.963	0.945	0.988
0.808	0.839	41.44	1.053	2.195	0.945	0.989
0.946	0.940	41.28	1.004	2.908	0.944	0.993

Table III. Results of the Consistency Test

system	T, K	Δy_1[a]
ethyl formate (1)-carbon tetrachloride (2)	318.15	0.003
ethyl formate (1)-chlorobenzene (2)	323.15	0.001
ethyl formate (1)-toluene (2)	318.15	0.003
ethyl formate (1)-acetonitrile (2)	323.15	0.005
chloroform (1)-toluene (2)	318.15	0.004
acetonitrile (1)-1-propanol (2)	328.15	0.005

[a] $\Delta y_1 = \Sigma |y_1(\text{exptl}) - y_1(\text{calcd})|/n$, where n = number of experimental points.

Table IV. Parameters of the UNIQUAC Equation (Anderson and Prausnitz's Modification) and Variance of Fit

system	temp, K	no. of data points	a_{12}, K	a_{21}, K	σ_F^2[a]
ethyl formate (1)-carbon tetrachloride (2)	318.15	12	−65.67	161.78	4.25
ethyl formate (1)-chlorobenzene (2)	323.15	12	−107.12	153.34	1.88
ethyl formate (1)-toluene (2)	318.15	9	7.05	25.93	5.61
ethyl formate (1)-acetonitrile (2)	323.15	8	140.07	−73.74	4.60
chloroform (1)-toluene (2)	318.15	7	−197.12	243.92	4.05
acetonitrile (1)-1-propanol (2)	328.15	10	469.77	23.62	5.45

[a] σ_F^2 = (sum of squared, weighted residuals)/(number of degrees of freedom).

and chloroform were subjected to purification. 1-Propanol was distilled in a 1.2-m glass column packed with McMahon packing after storage over copper sulfate anhydride. Chloroform was shaken with concentrated sulfuric acid to remove alcohol impurities, then with dilute sodium hydroxide, and finally with distilled water. It was dried over calcium sulfate, stored in the dark in an atmosphere of dry nitrogen, and distilled shortly before use. The densities and refractive indices of the materials used for experimental work are listed in Table I together with literature values.

Apparatus. A Boublík still was used to obtain vapor-liquid equilibrium data. The details of the still and experimental techniques have been described previously (*10*). Minor modifications were vapor and liquid sample receivers with magnetic stirrers to mix well the samples. Vapor and liquid samples for the system ethyl formate-acetonitrile were analyzed by using an Anton Paar (DMA-40) digital density meter and those for the system chloroform-toluene by a Shimadzu (GC-7A) gas chromatograph connected to a Shimadzu (ITG-2A) digital integrator. Analyses of the samples for the other systems were made by measuring their refractive indices with a Shimadzu Pulfrich refractometer.

Experimental Results and Data Analysis

Table II presents isothermal vapor-liquid equilibrium data for the six binary systems. Only the system acetonitrile-1-propanol forms an azeotrope at 41.48 kPa and 0.885 mole fraction of acetonitrile at 328.15 K. The liquid-phase activity coefficients were calculated by taking vapor-phase nonideality into account in accordance with the methods of Prausnitz et al. (*12*).

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

where the vapor pressures of pure components were obtained from the Antoine equation: ethyl formate and chloroform (*2*); carbon tetrachloride, toluene, and 1-propanol (*13*); chlorobenzene (*5*); acetonitrile (*3*). Pure-component second virial coefficients and cross coefficients were estimated by the method of Hayden and O'Connell (*7*) to calculate the vapor-phase fugacity coefficients. Further details of the calculations of eq 1 are given elsewhere (*12*).

Thermodynamic consistency of the observed P-x-y data was tested by using the method of orthogonal collocation suggested by Christiansen and Fredenslund (*4*). The results for the

Table V. UNIFAC Group-Interaction Parameters and Root-Mean-Square Deviations for Binary Systems

m/n	group-interaction parameters, K		ref systems (component 1-component 2)	temp, K	rmsd[a]		data source
	a_{mn}	a_{nm}			$10^3(\Delta y_1)$	ΔP, kPa	
ACH/HCOO	−71.33	876.1	ethyl formate-benzene	323.15	8	0.37	*11*
			ethyl formate-benzene	316.85-334.55	6	0.59	*11*
$ACCH_2$/HCOO	89.46	1638	ethyl formate-toluene	318.15	9	0.43	this work
CCl_4/HCOO	409.1	30.59	ethyl formate-carbon tetrachloride	318.15	4	0.24	this work
ACCl/HCOO	−89.82	1772	ethyl formate-chlorobenzene	323.15	6	0.93	this work
CCN/HCOO	56.24	−46.38	ethyl formate-acetonitrile	323.15	5	0.18	this work
$ACCH_2/CCl_3$	−139.3	229.4	chloroform-toluene	318.15	4	0.19	this work
CCOH/CCN	171.7	50.96	ethanol-acetonitrile	293.15	15	0.43	*8*
			ethanol-acetonitrile	343.15	12	1.62	*8*
			ethanol-acetonitrile	393.15	31	31.36	*8*
			acetonitrile-ethanol	313.15	10	0.64	*15*
			acetonitrile-1-propanol	328.15	9	0.60	this work
			acetonitrile-2-propanol	323.15	6	0.16	*9*
OH/CCN	141.3	140.6	ethanol-acetonitrile	293.15	12 (48)[b]	0.36 (1.16)[b]	*8*
			ethanol-acetonitrile	343.15	12 (19)	1.88 (4.51)	*8*
			ethanol-acetonitrile	393.15	31 (8)	31.05 (3.57)	*8*
			acetonitrile-ethanol	313.15	7 (39)	0.54 (2.31)	*15*
			acetonitrile-1-propanol	328.15	8 (41)	0.76 (3.14)	this work
			acetonitrile-2-propanol	323.15	4 (32)	0.20 (2.53)	*9*

[a] rmsd = $[\Sigma(X_{\text{exptl}} - X_{\text{calcd}})^2/n]^{1/2}$, where X is y_1 or P and n is the number of experimental points. [b] Calculated from the parameters in the table of ref *14*.

six binary systems are shown in Table III, indicating that the experimental data are thermodynamically consistent.

The modified UNIQUAC equation suggested by Anderson and Prausnitz (*1*, *12*) was used to correlate the experimental vapor-liquid equilibrium data. This equation presents the activity coefficients as follows:

$$\ln \gamma_1 = \ln (\phi_1/x_1) + (Z/2)q_1 \ln (\theta_1/\phi_1) + \phi_2[l_1 - (r_1/r_2)l_2] - q_1' \ln (\theta_1' + \theta_2'\tau_{21}) + \theta_2'q_1'[\tau_{21}/(\theta_1' + \theta_2'\tau_{21}) - \tau_{12}/(\theta_2' + \theta_1'\tau_{12})] \quad (2a)$$

$$\ln \gamma_2 = \ln (\phi_2/x_2) + (Z/2)q_2 \ln (\theta_2/\phi_2) + \phi_1[l_2 - (r_2/r_1)l_1] - q_2' \ln (\theta_2' + \theta_1'\tau_{12}) + \theta_1'q_2'[\tau_{12}/(\theta_2' + \theta_1'\tau_{12}) - \tau_{21}/(\theta_1' + \theta_2'\tau_{21})] \quad (2b)$$

where

$$\phi_1 = x_1r_1/(x_1r_1 + x_2r_2) \qquad \phi_2 = x_2r_2/(x_1r_1 + x_2r_2) \quad (3)$$

$$\theta_1 = x_1q_1/(x_1q_1 + x_2q_2) \qquad \theta_2 = x_2q_2/(x_1q_1 + x_2q_2) \quad (4)$$

$$\theta_1' = x_1q_1'/(x_1q_1' + x_2q_2') \qquad \theta_2' = x_2q_2'/(x_1q_1' + x_2q_2') \quad (5)$$

$$l_1 = (Z/2)(r_1 - q_1) - (r_1 - 1) \qquad l_2 = (Z/2)(r_2 - q_2) - (r_2 - 1) \quad (6)$$

$$\tau_{12} = \exp(-\Delta u_{12}/RT) \equiv \exp(-a_{12}/T) \qquad \tau_{21} = \exp(-\Delta u_{21}/RT) \equiv \exp(-a_{21}/T) \quad (7)$$

For 1-propanol $q' = 0.89$ and for the other pure components $q_i' = q_i$ (*1*, *12*). Computer programs described in the monograph of Prausnitz et al. (*12*) were used to find the reliable UNIQUAC binary parameters. The numerical values of the binary parameters for the systems are listed in Table IV with the estimated variance of the fit.

Determination of UNIFAC Group-Interaction Parameters

The UNIFAC group-interaction parameter table of Skjold-Jørgensen et al. (*14*) provides us with a useful tool for predicting vapor-liquid equilibria for systems where experimental data are not available, and there are some of the missing parameters because of lack of reliable experimental data.

To extend and revise the UNIFAC group-interaction parameter table of Skjold-Jørgensen et al., we determined the new parameters based on the present experimental data in accordance with the method of Fredenslund et al. (*6*). Table V gives the values of the group-interaction parameters and the root-mean-square deviations (rmsd) in vapor mole fraction and total pressure for the reference systems.

Acknowledgment

We are grateful to the Data Processing Center, Kanazawa University, for the use of its facilities. T. Morita, K. Hirose, and E. Aust assisted with the experimental work.

Glossary

a_{ij}	UNIQUAC binary interaction parameter defined by $\Delta u_{ij}/R$, K
l_i	pure-component constant defined by eq 6
P	total pressure, kPa
P_i^s	vapor pressure of pure component i, kPa
q_i	molecular-geometric area parameter for component i
q_i'	molecular-interaction area parameter for component i
r_i	molecular volume parameter for pure component i
R	gas constant, 8.314 J/(mol K)
T	absolute temperature, K
Δu_{ij}	UNIQUAC binary interaction parameter, J/mol
v_i^L	liquid molar volume of pure component i, cm^3/mol
x_i	liquid-phase mole fraction of component i
y_i	vapor-phase mole fraction of component i
Z	lattice coordination number, a constant set equal to 10

Greek Letters

γ_i	activity coefficient of component i
θ_i	area fraction defined by eq 4
θ_i'	area fraction defined by eq 5
σ_F^2	variance of fit
τ_{ij}	UNIQUAC binary parameter
ϕ_i	volume fraction defined by eq 3
ψ_i	fugacity coefficient of component i
ψ_i^s	fugacity coefficient of pure component i at system temperature and P_i^s

J. Chem. Eng. Data 1983, 28, 39-45

Subscripts

i component

Superscripts

s saturation

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Received for review February 16, 1982. Accepted July 2, 1982.

Enthalpies of Formation, Densities, and Heat Capacities at 25 °C in the Liquid-Phase Region of the System $K_2O-P_2O_5-H_2O$

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Measurements of the enthalpies of solution of monopotassium orthophosphate in various aqueous solutions of potassium hydroxide and phosphoric acid were made at 25 °C, and the apparent enthalpies of formation of the solutions were derived. Measurements of the densities and heat capacities of the solutions also were made.

The heat requirements in the production of fertilizer solutions may be determined by measurement of the enthalpies of formation of solutions of different $K_2O:P_2O_5$ ratios in the liquid-phase region of the system $K_2O-P_2O_5-H_2O$. This information also would be helpful in determining both the enthalpies of hydrolysis of potassium polyphosphate solutions and the enthalpies of formation of solutions containing additional components such as ammonia, urea, and chloride.

Reported here are the results of measurements of the enthalpies of solution of KH_2PO_4 in various aqueous solutions of KOH and H_3PO_4. The enthalpies of solution were combined with published values of enthalpies of formation to determine the enthalpies of formation of the solutions. The densities and the heat capacities of the solutions also are reported. Enthalpies of solution of H_3PO_4 (*1*), KH_2PO_4 (*2*), and K_2HPO_4 (*3*) have been reported. These data may be combined with published values of the enthalpies of formation of $H_3PO_4 \cdot 100H_2O$ (*4*), KH_2PO_4, and K_2HPO_4 (*5*) to derive the enthalpies of formation of orthophosphate solutions with mole ratios of $K_2O:P_2O_5$ of 0, 1, and 2.

Materials and Apparatus

Monopotassium orthophosphate was prepared by recrystallizing the reagent-grade salt from distilled water and drying at 105 °C. Chemical analyses showed this salt to contain 52.1% P_2O_5 and 34.6% K_2O (stoichiometric; 52.15% P_2O_5, 34.61% K_2O). The potassium hydroxide solutions were prepared from reagent-grade KOH and distilled water. Their concentrations, expressed in molality (m_1), were determined by acid titrations. The phosphoric acid solutions were prepared from reagent-grade H_3PO_4 and distilled water. Their concentrations, also expressed in molality (m_2), were determined by chemical analyses.

The solution calorimeter, the method of measurement, and the corrections applied have been described (*6*, *7*). The defined calorie was taken as 4.1840 absolute J. The average temperature for each of the solution periods is listed in the supplementary material (see paragraph at end of text regarding supplementary material). No corrections were applied to convert the enthalpies of solution to 25.00 °C.

Enthalpies of Solution of KH_2PO_4 in KOH Solutions

Monopotassium orthophosphate was added to each of the KOH solutions in successive increments to a final concentration near the saturation isotherm (*8*). The maximum temperature change during the solution period was arbitrarily set at about 1 °C, which limited the amount of solute to about 8 g at the lower concentrations of KH_2PO_4. The bulb volumes limited the amount of solute at the higher concentrations. The transfer of the final solution of one measurement from the calorimeter to a weighed fixed volume for the next measurement entailed some loss of the solution. Where larger amounts of solute were dissolved, there was still an excess of solution after the transfer and the excess could be removed before weighing the initial solution for the next measurement. Where smaller amounts of solute were dissolved, however, it was necessary to weigh the transferred solution and then add a weighed amount of the solvent (the KOH solution) to maintain the fixed volume. The concentration of the initial solution for the measurement thus could be determined. The concentration for each measurement, expressed as molality of KH_2PO_4 (m_2), is the average concentration of the initial and final solutions. The differential enthalpy of solution for each measurement was calculated from the equation

$$dT/dm_2 = 136.08934Q/1000w \qquad (1)$$

where Q is the observed enthalpy change in calories, w is the