J. Chem. Eng. Data 1989, 34, 375-382 375

Effect of Dissolved Salts on the Heat of Mixing of Three Binary Systems

M. Rajendran, S. Renganarayanan, P. R. Madhavan,[†] and D. Srinivasan*

Department of Chemical Engineering, A. C. College of Technology, Anna University, Madras 600 025, India

The effect of three dissolved inorganic salts, namely sodium chloride, calcium chloride, and zinc chloride on the heat of mixing (both endothermic and exothermic) of three binary miscible systems, namely, methanol (1)-water† (2) (exothermic), methanol† (1)-benzene (2) (endothermic) and pyridine (1)-water† (2) (exothermic), has been experimentally investigated. The salts were dissolved in the solvent (in which they are preferentially soluble, indicated by the superscript †) to concentrations up to 20% by weight wherever possible. The experimentation was done at 30 °C using a standard-type calorimeter attached to a microprocessor-based control unit MIPROC following established experimental procedure. The unit MIPROC was designed in our laboratory. In the case of methanol-water system the salt sodium chloride decreased the exothermic values steadily as its concentration was increased while the salt calcium chloride was found to shift the heat of mixing values to the positive side. Similarly, the salts calcium chloride and zinc chloride entailed an increase in the endothermic heat of mixing of the methanol-benzene system. As for the system pyridine-water, the exothermic heat of mixing values were enhanced upon addition of these three salts.

Introduction

An important technique in extractive distillation is the use of inorganic salts as extractive agents to modify the relative volatility of the binary mixture. The selective effect that a salt can have on the volatilities of two liquid components and hence on the composition of the equilibrium vapor comes about primarily through the effect exerted by salt ions and/or molecules on the structure of the liquid phase (*1*, *2*). The most likely effect is that salt would induce the formation of associated complexes or clusters of molecules of the volatile component about its ions (*3*). The salt effect is also believed (*4*) to be a complex function of salt and solvent interaction and self-interaction among all the components of the system (*5*).

An equation has been derived (*6*) that indicates the changes in the chemical potentials of the solvent components when a salt is added to a mixed solvent. Studies on heat of solutions of electrolytes in nonaqueous-aqueous solvent mixtures have been limited mostly to alcohol-water systems (*7*). Upon addition of electrolytes to liquid mixtures, appreciable change in the free energy of the liquid component is expected. Since excess free energy and excess enthalpy of liquid mixtures are interrelated, addition of salt can be expected to influence the heat of mixing values of the two liquid components when mixed. It is, therefore, of academic curiosity to investigate the effect of dissolved salts on heat of mixing of liquid mixtures.

In this investigation the effect of three dissolved inorganic salts, namely, sodium chloride, calcium chloride, and zinc chloride, on the heat of mixing of the binary systems methanol (1)-water† (2), methanol† (1)-benzene (2), and pyridine (1)-water† (2) has been studied experimentally. The experimentation was done at 30 ± 1 °C, at which the losses due to vaporization were taken to be insignificant in the case of the methanol-water† and pyridine-water† systems while the heat of evaporation effect has not been taken into account in the case of the nonaqueous system, namely, methanol†-benzene. A calorimeter connected to a microprocessor-based control unit (viz., MIPROC digital calorimeter) that was designed in our laboratory has been used. The description of the apparatus, experimental technique, and correlation of the experimentally determined heat of mixing data have been detailed below.

Table I. Physical Properties of Pure Components at 30 °C

component	boiling point, °C this work	boiling point, °C lit. (*8*)	specific gravity, g/cm^3 this work	specific gravity, g/cm^3 lit. (*8*)	refractive index this work	refractive index lit. (*8*)
methanol	64.90	64.80	0.7826	0.7820	1.3251	1.3244
benzene	80.50	80.10	0.8678	0.8690	1.4952	1.5011
pyridine	116.00	115.25	0.9850	0.9832	1.5102	1.4984
water	100.00	100.00	0.9982	0.9988	1.3310	1.3330

Experimental Section

Chemicals. The components, both solvents and salts, used in the present investigation were of analytical reagent grade. The solvents were further purified by fractional distillation, and the salts were dried before use. The physical properties of the components used have been checked with the corresponding literature values (*8*) and were found to be in close proximity (Table I).

Experimental Apparatus. The calorimeter used in this work is basically of the same type used by Tsao and Smith (*9*) and Murti and van Winkle (*10*). The calorimeter is essentially a double-walled Dewar flask of 215 cm^3 volume. The cell is connected a microprocessor which has an EPROM loaded with the program to convert the heat energy (volts × amperes) supplied to the liquid mixture into a direct display as calories. A resistant thermometer device attached to the calorimeter is connected to the microprocessor to measure the temperature changes when the solvents are mixed. The values displayed by the microprocessor have been checked by performing the conventional method of calculating heat of mixing values. In this investigation the heat of mixing data have been obtained by the use of the MIPROC system. Figure 1 shows the schematic diagram of the calorimeter used.

Microprocessor Design Details. The MIPROC digital calorimeter is a microprocessor-based instrument with the capacity to handle 10 analogue input channels. It was designed in our laboratory and was constructed by M/s. Precision Instrument and Electronics (Madras) Private Limited. It is designed to measure the heat equivalents in calories due to either endothermic or exothermic process between the two liquids when mixed. The operations of the system are directed by the control program that is stored in an alternate EPROM chip. The system can never become obsolete as any adjustments or changes required in future can be made by changing the program in the EPROM.

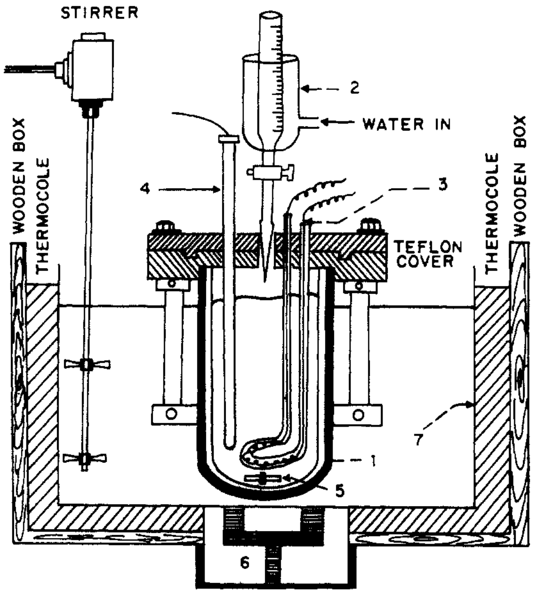
The MIPROC digital calorimeter is programmed to monitor and display the output voltage and heater current. It computes

---

[†] Presently a Chartered Engineer, 2, Deivasigamani Street, Royapettah, Madras 600 004, India.

* To whom correspondence should be addressed.

0021-9568/89/1734-0375$01.50/0



1. DOUBLE-WALLED DEWAR'S FLASK (INSULATED)
2. INSULATED JACKETED BURETTE
3. PLATINUM HEATING ELEMENT
4. RESISTANCE THERMOMETER
5. TEFLON COATED IRON PIECE
6. MAGNETIC STIRRER
7. DOUBLE INSULATED CONSTANT TEMPERATURE BATH APPARATUS

Figure 1. Schematic diagram of experimental apparatus.

the heat of mixing values in calories through the heat elements using the formula

$$Q = VIt/4.184 \text{ cal}$$

where V is the resistance across the heater in volts, I is the current passing through the heater in amperes, and t is the time in seconds. The calories are calculated and displayed in steps of 0.1 cal in the range of 0–9999.9 cal.

This instrument has a built-in regulated power supply which can be adjusted to any voltage up to 20 V dc at a maximum of 2.0 A. The system is provided with a real-time clock, and hence the time used in the above formula is measured to the accuracy of 0.1 s. The instrument shows the voltage and current in steps of 0.01 V and 0.001 A, respectively. The system is also provided with a signal-conditioning electronic device to connect a resistance thermometer device (RTD) and displays the temperature when the RTD probe lead from the calorimeter is connected. The temperature will be displayed in steps of 0.01 °C in the range of 0–99.99 °C.

Accuracy of the Calorimeter. The performance of the calorimeter and its reliability for the measurement of heat of mixing values were ascertained by measuring the heat of mixing values of the non-salt system, benzene (1)–cyclohexane (2), at 30 °C. The data obtained in the present work (Figure 2) compared well within 2% with the literature data (*14*).

Preparation of the Salt Solution. In this investigation, the salts studied were first dissolved in the component (in which they are preferentially soluble) to the desired level of concentration. For example, in the methanol (1)–water (2)–sodium chloride system, the concentration values reported, namely, 5%, 10%, etc., are concentrations by weight (weight of salt/weight of (salt + water)) in the water component and the salt solution thus prepared was taken either in the buret or in the calorimeter depending upon the situation with respect to the concentration range. In other words, by measuring the values of the heat of mixing for the system methanol–5% NaCl solution, the effect of 5% NaCl on the values of heat of mixing of methanol–water† is ascertained. The same procedure was adopted in the case of the nonaqueous binary system, namely, methanol† (1)–benzene (2).

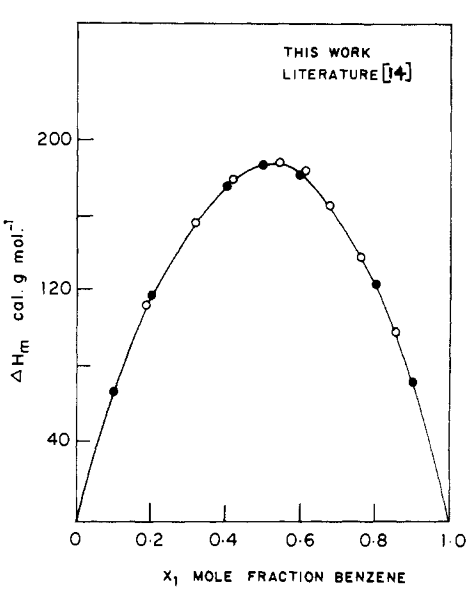


Figure 2. Comparison of heat of mixing at 30 °C. System: benzene (1)–cyclohexane (2).

Experimental Method. About 100 cm^3 of one of the components to be mixed was introduced from a calibrated buret into the calorimeter, and the second component was placed in a thermally insulated jacketed buret. This buret was fixed on the top lid of the calorimeter chamber so as to facilitate the controlled metering of the second component into the calorimeter. The whole assembly of the calorimeter was placed in a constant-temperature bath whose temperature was controlled by a special relay circuit, and the water from this bath was circulated through the jacket of the buret in order to minimize the heat losses due to temperature changes. As mentioned earlier, this buret itself was insulated to prevent any heat loss to the atmosphere. Sufficient time (1–1.5 h) was allowed for the second component in the jacketed buret to attain the desired level of the temperature. The entire experimental set up was kept in a wooden box lined with thermocole internally to minimize the errors due to loss of heat through ambience.

By operating the heating element, the temperature of the liquid component in the calorimeter was also brought to the desired value. When both components were at the desired temperature, a known amount of the second component from the buret was then added slowly. The magnetic stirrer was set in motion (approximately at 80 rpm), and the drop or rise in temperature was recorded in the MIPROC system. If a drop in temperature was observed, the heater circuit in the MIPROC system was turned on in order to bring the temperature back to the original experimental temperature. If a rise in temperature was observed, the whole system was allowed to cool to the original experimental temperature and then the MIPROC system was switched on to get the temperature attained after mixing.

During the course of a run, about five to six readings were taken after each successive addition of the liquid component from the buret. To cover the other concentration range, the second component was taken in the calorimeter and the first was added from the buret. The MIPROC unit (which is designed to give the value Q (= $VIt/4.184$) in calories) directly displays the value which when divided by the total number of moles of liquid mixture taken gives the heat of mixing values ΔH in calories per mole. The experiment for each system was re-

Table II. Heat of Mixing Data for the System Methanol (1)–Water† (2) at 30 °C. Salt: Sodium Chloride

no salt				5% NaCl					10% NaCl				
x_1	ΔH^{M}_{exp}	ΔH^{M}_{cal}	dev[a]	x_1	salt concn, wt %	ΔH^{M}_{exp}	ΔH^{M}_{cal}	dev[a]	x_1	salt concn, wt %	ΔH^{M}_{exp}	ΔH^{M}_{cal}	dev[a]
0.029	−48.5	−48.6	−0.1	0.082	4.340	−70.0	−70.0	0.0	0.055	9.150	−40.0	−41.0	−1.0
0.103	−138.7	−137.8	0.9	0.122	4.050	−100.3	−100.4	−0.1	0.070	8.930	−52.7	−51.8	0.9
0.205	−199.5	−201.2	−1.7	0.244	3.240	−162.5	−161.8	0.7	0.130	8.070	−92.6	−90.6	2.0
0.386	−214.7	−213.3	1.4	0.341	2.670	−178.3	−177.2	1.1	0.210	7.020	−127.0	−128.1	−1.1
0.597	−162.2	−162.9	−0.7	0.412	2.290	−172.1	−173.9	−1.8	0.299	5.940	−142.0	−148.8	−6.8
0.768	−111.9	−111.9	0.0	0.504	1.840	−157.6	−158.0	−0.4	0.358	5.280	−161.8	−152.0	9.8
0.822	−94.3	−94.0	0.3	0.560	1.590	−141.6	−144.8	−3.2	0.455	4.280	−138.7	−144.2	−5.5
0.953	−33.2	−33.2	0.0	0.680	1.380	−135.0	−132.3	2.7	0.536	3.510	−129.0	−130.2	−1.2
				0.730	0.898	−100.0	−97.9	2.1	0.660	2.430	−109.0	−103.1	5.9
				0.805	0.627	−75.0	−74.4	0.6	0.743	1.770	−80.4	−82.6	2.2
				0.894	0.328	−40.0	−42.6	−2.6	0.871	0.847	−44.0	−45.0	−1.0
				0.940	0.182	−25.4	−24.5	0.9	0.942	0.371	−20.7	−20.4	0.3

15% NaCl					20% NaCl				
x_1	salt concn, wt %	ΔH^{M}_{exp}	ΔH^{M}_{cal}	dev[a]	x_1	salt concn, wt %	ΔH^{M}_{exp}	ΔH^{M}_{cal}	dev[a]
0.058	13.72	−37.4	−36.8	0.6	0.110	17.00	−55.0	−55.3	−0.3
0.176	11.34	−91.2	−97.1	−5.9	0.213	14.44	−95.0	−92.9	2.1
0.258	9.83	−125.5	−122.8	2.7	0.257	13.40	−100.4	−101.9	−1.5
0.290	9.27	−130.6	−128.9	1.7	0.300	12.43	−106.4	−106.7	−0.3
0.328	8.63	−136.5	−133.6	2.9	0.432	9.60	−100.7	−101.5	−0.8
0.364	8.04	−140.0	−135.3	4.7	0.500	8.26	−90.0	−91.2	−1.2
0.404	5.93	−133.4	−134.4	−1.0	0.591	6.55	−77.6	−73.9	3.7
0.500	5.97	−115.0	−121.8	−6.8	0.680	4.97	−55.0	−55.7	−0.7
0.690	3.47	−69.2	−70.2	−1.0	0.708	4.50	−48.5	−49.8	−1.3
0.773	2.44	−47.0	−44.9	2.1	0.806	2.89	−30.0	−29.2	0.8
0.856	1.50	−23.6	−22.9	0.7	0.860	2.05	−17.5	−18.1	−0.6
0.916	0.86	−10.0	−10.5	−0.5	0.931	0.99	−5.8	−5.7	0.1

[a] ($\Delta H^{M}_{cal} - \Delta H^{M}_{exp}$).

Table III. Heat of Mixing Data for the System Methanol (1)–Water† (2) at 30 °C. Salt: Calcium Chloride

no salt				5% $CaCl_2$					10% $CaCl_2$				
x_1	ΔH^{M}_{exp}	ΔH^{M}_{cal}	dev[a]	x_1	salt concn, wt %	ΔH^{M}_{exp}	ΔH^{M}_{cal}	dev[a]	x_1	salt concn, wt %	ΔH^{M}_{exp}	ΔH^{M}_{cal}	dev[a]
0.029	−48.5	−48.6	−0.1	0.120	4.06	272.7	268.4	4.3	0.120	8.21	259.6	264.9	5.3
0.103	−138.7	−137.8	0.9	0.181	3.64	302.5	313.4	10.9	0.181	7.38	344.5	327.6	−16.9
0.205	−199.5	−201.2	−1.7	0.310	2.84	345.0	342.3	−3.3	0.310	5.82	328.4	357.7	29.3
0.386	−214.7	−213.3	1.4	0.389	2.41	350.2	340.0	−10.2	0.389	4.95	332.6	328.3	−4.3
0.597	−162.2	−162.9	−0.7	0.483	1.94	328.2	319.9	−8.3	0.483	4.00	294.0	282.9	−11.1
0.768	−111.7	−111.9	−0.2	0.561	1.58	276.1	287.2	11.1	0.561	3.28	262.4	244.1	−18.3
0.822	−94.3	−94.0	0.3	0.610	1.37	250.2	260.2	10.0	0.610	2.86	200.3	221.4	21.1
0.953	−33.2	−33.2	0	0.793	0.67	155.5	147.1	−8.4	0.793	1.40	144.1	142.8	−1.3
				0.894	0.33	90.7	92.7	2.0	0.894	0.69	86.4	86.4	0.0

[a] ($\Delta H^{M}_{cal} - \Delta H^{M}_{exp}$).

Table IV. Heat of Mixing Data for the System Methanol (1)–Water† (2) at 30 °C. Salt: Zinc Chloride

no salt				5% $ZnCl_2$					10% $ZnCl_2$				
x_1	ΔH^{M}_{exp}	ΔH^{M}_{cal}	dev[a]	x_1	salt concn, wt %	ΔH^{M}_{exp}	ΔH^{M}_{cal}	dev[a]	x_1	salt concn, wt %	ΔH^{M}_{exp}	ΔH^{M}_{cal}	dev[a]
0.029	−48.5	−48.6	−0.1	0.100	4.210	−132.0	−131.7	0.3	0.100	8.490	−140.0	−139.6	0.4
0.103	−138.7	−137.7	1.0	0.150	3.850	−164.0	−164.3	−0.3	0.150	7.800	−172.0	−173.6	−1.6
0.205	−199.5	−201.2	−1.7	0.200	3.510	−186.0	−185.2	0.8	0.200	7.140	−194.0	−193.5	0.5
0.386	−214.7	−213.3	1.4	0.250	3.200	−194.0	−198.5	−4.5	0.250	6.520	−202.0	−203.8	−1.8
0.597	−162.2	−162.9	−0.7	0.300	2.900	−210.0	−206.8	3.2	0.300	5.930	−215.0	−207.8	7.2
0.768	−111.7	−111.9	−0.2	0.400	2.350	−215.0	−211.7	3.3	0.400	4.840	−200.0	−204.6	−4.6
0.822	−94.3	−94.0	0.3	0.500	1.860	−200.0	−202.8	−2.8	0.500	3.850	−190.0	−193.7	−3.7
0.953	−33.2	−33.2	0.0	0.600	1.415	−182.0	−181.6	0.4	0.600	2.940	−180.0	−179.6	0.4
				0.700	1.010	−150.0	−152.9	−2.9	0.700	2.200	−170.0	−163.8	6.2
				0.800	0.645	−125.0	−121.4	3.6	0.800	1.350	−140.0	−142.7	−2.7
				0.900	0.308	−80.0	−81.5	−1.5	0.900	0.649	−100.0	−100.9	−0.9
				0.950	0.151	−50.0	−49.7	0.3	0.950	0.318	−62.0	−61.6	0.4

[a] ($\Delta H^{M}_{cal} - \Delta H^{M}_{exp}$).

peated to check the reproducibility of the data which were found to be within 3% error.

Results

The experimental heat of mixing data obtained in this investigation for these three systems under various salt conditions are given in the form of tables and also represented graphically as detailed below. The compositions of liquid mixtures are expressed in mole fraction on a salt-free basis. It should be mentioned in this context that the salt concentrations indicated in the headings of each table refer to the initial concentrations of the salts in the component in which they are preferentially

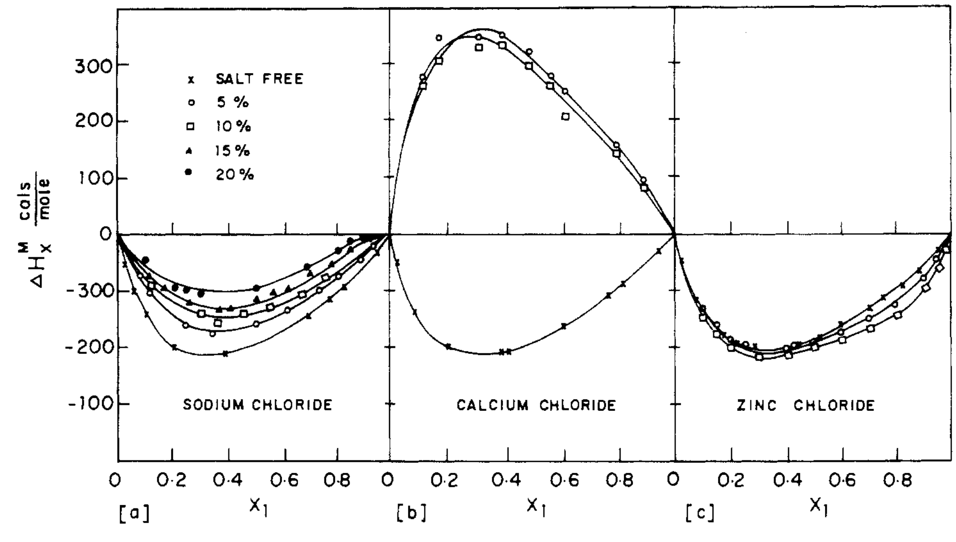


Figure 3. Effect of salt on heat of mixing. System: methanol (1)-water (2). (a) NaCl; (b) $CaCl_2$; (c) $ZnCl_2$. Temperature 30 °C. x_1 = mole fraction of methanol. Concentration of salt (in wt %) in water before mixing.

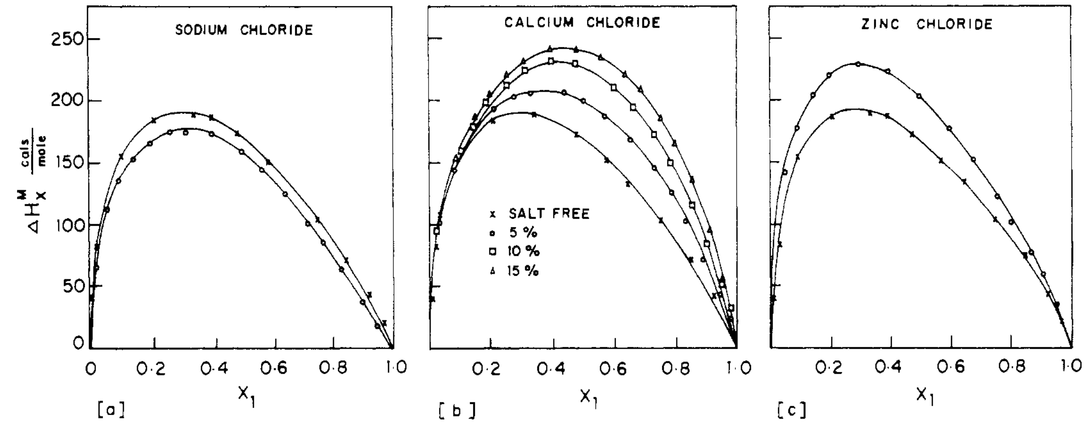


Figure 4. Effect of salt on heat of mixing. System: methanol (1)-benzene (2). (a) NaCl; (b) $CaCl_2$; (c) $ZnCl_2$. Temperature 30 °C. x_1 = mole fraction of methanol. Concentration of salt (in wt %) in methanol before mixing.

soluble. Also given in the tables are the true salt concentrations in the final mixture.

***System*: *Methanol (1)-Water*[†] *(2)*.** The experimental heat of mixing data at 30 °C are given in Tables II-IV and are presented graphically in Figure 3, which also shows the heat of mixing data obtained in this investigation under the no-salt condition.

Of the three salts studied, sodium chloride and zinc chloride do not change the normal behavior of the heat of mixing although the former shows a pronounced effect on the magnitude of the heat of mixing, toward the positive side. The calcium chloride salt has been found to give a strikingly opposite effect in that the heat of mixing values move to the positive side, thereby showing endothermic behavior for this system which is exothermic under the no-salt condition. The salt calcium chloride has been found to bring about a large variation in the values of the enthalpy of mixing at a concentration of 5%. However, a further increase in the concentration (10%) of $CaCl_2$ does not bring out any additional significant change in the heat of mixing values. A similar phenomenon has been observed in our study on salt effect in vapor-liquid equilibria of the methanol-water system which forms part of our ongoing program in salt effect on VLE, LLE, and heat of mixing. While addition of sodium chloride and zinc chloride at a few concentrations does not show any significant variations in the values of relative volatility, the salt calcium chloride when added in different concentrations has been found to influence the VLE to a large extent. The concentration of calcium chloride and zinc chloride could not be studied beyond 10% because of the difficulties in experimentation as the addition of salt in a larger quantity resulted in precipitation of the salt when the methanol component was added to the salt solution in the calorimeter.

***System*: *Methanol*[†] *(1)-Benzene (2)*.** The experimental heat of mixing data at 30 °C are given in Tables V-VII and are shown graphically in Figure 4. The salt sodium chloride, which is preferentially soluble in methanol, decreases the endothermic values of the heat of mixing throughout the liquid composition of methanol (Figure 4a). For the salt calcium chloride the increase in heat of mixing values is negligible up to 0.2 mole fraction of methanol but the values increase appreciably thereafter (Figure 4b). The salt zinc chloride could be added only up to 5%, which resulted in saturation. The heat of mixing values for this salt (Figure 4c) almost coincided with those data obtained with 10% calcium chloride salt.

***System*: *Pyridine (1)-Water*[†] *(2)*.** For this system, which shows exothermicity in the heat of mixing, the addition of the three salts results in an increase in exothermicity. Furthermore, the salts sodium chloride and zinc chloride could be added in larger concentrations without any problems like precipitation as compared to the other systems. The largest increase on the exothermic side has been observed in the case of calcium chloride. However, the change in values of the heat of mixing in the presence of the salts calcium chloride and zinc chloride are not significant. Moreover, a peculiar phenomenon has been observed upon the addition of sodium chloride. This salt increases the exothermicity at low concentration (5%) but de-

Table V. Heat of Mixing Data for the System Methanol† (1)–Benzene (2) at 30 °C. Salt: Sodium Chloride

no salt				5% NaCl				
x_1	ΔH^M_{exp}	ΔH^M_{cal}	dev[a]	x_1	salt concn, wt %	ΔH^M_{exp}	ΔH^M_{cal}	dev[a]
0.016	40.0	43.3	3.4	0.030	0.066	66.2	67.3	1.1
0.030	82.0	73.8	-8.2	0.055	0.123	112.0	106.1	-5.9
0.102	155.0	163.3	8.3	0.091	0.207	135.2	141.8	6.6
0.212	186.1	189.2	3.1	0.188	0.455	164.4	171.4	7.0
0.337	190.0	182.9	7.1	0.262	0.664	174.0	170.1	-3.9
0.395	187.5	179.9	-7.6	0.308	0.806	175.0	168.3	-6.7
0.474	173.0	174.1	1.1	0.390	1.080	174.8	166.6	-8.2
0.581	150.4	155.8	5.4	0.487	1.450	159.0	162.7	3.7
0.644	133.0	137.9	4.9	0.560	1.750	144.8	152.7	7.9
0.748	102.4	102.2	-0.2	0.714	2.690	102.0	105.2	3.2
0.850	72.0	68.4	-3.6	0.831	3.400	65.0	69.6	4.6
0.971	20.0	20.3	0.3	0.950	4.460	19.6	20.3	0.7

[a] $(\Delta H^M_{cal} - \Delta H^M_{exp})$.

Table VI. Heat of Mixing Data for the System Methanol† (1)–Benzene (2) at 30 °C. Salt: Calcium Chloride

no salt				5% $CaCl_2$				
x_1	ΔH^M_{exp}	ΔH^M_{cal}	dev[a]	x_1	salt concn, wt %	ΔH^M_{exp}	ΔH^M_{cal}	dev[a]
0.016	40.0	43.3	3.3	0.050	0.111	112.4	109.7	-2.7
0.030	82.0	73.8	-8.2	0.100	0.229	155.0	162.1	-2.9
0.102	155.0	163.3	8.3	0.150	0.354	180.0	183.3	3.3
0.212	186.1	189.2	3.1	0.200	0.487	192.4	189.9	-2.5
0.337	190.0	182.9	-7.1	0.300	0.781	206.6	194.7	-11.9
0.395	187.5	179.9	-7.6	0.400	1.110	207.0	203.5	-3.5
0.474	173.0	174.1	1.1	0.500	1.510	201.0	207.5	6.5
0.581	150.0	155.8	5.8	0.600	1.960	185.2	193.1	7.9
0.644	133.0	137.9	-4.9	0.700	0.510	158.4	158.7	0.3
0.748	102.4	102.2	-0.2	0.800	3.160	121.4	115.3	-6.1
0.850	72.0	68.4	-3.6	0.900	3.970	70.0	70.7	0.7
0.971	20.0	20.3	0.3	0.950	4.460	42.4	42.7	0.3

10% $CaCl_2$					15% $CaCl_2$				
x_1	salt concn, wt %	ΔH^M_{exp}	ΔH^M_{cal}	dev[a]	x_1	salt concn, wt %	ΔH^M_{exp}	ΔH^M_{cal}	dev[a]
0.050	0.234	115.0	112.7	-2.3	0.050	0.371	126.0	121.3	-4.7
0.100	0.482	162.0	166.9	4.9	0.100	0.764	165.0	174.5	9.5
0.150	0.745	185.0	189.9	4.9	0.150	1.170	180.0	193.1	13.1
0.200	1.020	200.0	199.4	-0.6	0.200	1.610	205.0	198.4	-6.6
0.300	1.630	224.8	211.6	-13.2	0.300	2.570	232.0	209.7	-22.3
0.400	2.330	232.4	228.0	-4.4	0.400	3.650	242.4	234.4	-8.0
0.500	3.130	229.0	236.3	7.3	0.500	4.880	241.0	253.1	12.1
0.600	4.06	212.0	221.7	9.7	0.600	6.290	230.0	244.5	14.5
0.700	5.150	185.0	183.9	-1.1	0.700	7.940	205.0	206.9	1.9
0.800	6.460	143.0	136.3	-6.7	0.800	9.880	164.6	155.9	-8.7
0.900	8.040	85.0	86.5	1.5	0.900	12.200	103.7	101.4	-2.3
0.950	8.960	53.0	53.0	-0.0	0.950	13.530	61.4	63.0	1.6

[a] $(\Delta H^M_{cal} - \Delta H^M_{exp})$.

Table VII. Heat of Mixing Data for the System Methanol† (1)–Benzene (2) at 30 °C. Salt: Zinc Chloride

no salt				5% $ZnCl_2$				
x_1	ΔH^M_{exp}	ΔH^M_{cal}	dev[a]	x_1	salt concn, wt %	ΔH^M_{exp}	ΔH^M_{cal}	dev[a]
0.0160	40.0	43.o	3.3	0.057	0.127	142.2	138.3	-3.9
0.030	82.0	73.8	-8.2	0.096	0.219	177.4	183.6	6.2
0.102	155.0	163.3	8.3	0.145	0.341	202.4	209.5	7.1
0.212	186.1	189.2	3.1	0.201	0.490	220.0	217.3	-2.7
0.337	190.0	182.9	-7.1	0.300	0.780	227.8	216.4	-11.4
0.395	187.5	179.9	-7.6	0.398	1.110	225.2	216.8	-8.4
0.474	173.0	174.1	1.1	0.500	1.500	202.0	210.8	8.8
0.581	150.0	155.8	5.8	0.600	1.960	176.4	186.3	9.9
0.644	133.0	137.9	4.9	0.682	2.400	150.1	152.3	2.2
0.748	102.4	102.2	-0.2	0.757	2.870	122.0	117.1	-4.9
0.850	72.0	68.4	-3.6	0.804	3.190	99.6	95.4	-3.2
0.971	20.0	20.3	0.3	0.956	4.520	33.0	33.5	0.5

[a] $(\Delta H^M_{cal} - \Delta H^M_{exp})$.

creases the exothermic behavior at higher concentrations. The experimental data for this system under different salt concentrations are given in Tables VIII–X and are shown in Figure 5.

Figure 6 shows the effect of these three salts on the equimolal composition values of the heat of mixing of the three systems.

Correlation of Experimental Heat of Mixing Data

The experimentally determined heat of mixing data for these salt-containing binary systems have been correlated by the Scatchard model. Scatchard et al. (*11*) have proposed an empirical equation based on an analogy of excess free energy

Table VIII. Heat of Mixing Data for the System Pyridine (1)–Water[†] (2) at 30 °C. Salt: Sodium Chloride

no salt				5% NaCl					10% NaCl				
x_1	ΔH^{M}_{exp}	ΔH^{M}_{cal}	dev^a	x_1	salt concn, wt %	ΔH^{M}_{exp}	ΔH^{M}_{cal}	dev^a	x_1	salt concn, wt %	ΔH^{M}_{exp}	ΔH^{M}_{cal}	dev^a
0.095	-357.5	-361.9	-4.4	0.100	3.420	-429.0	-432.6	-3.6	0.100	6.950	-430.4	-434.7	-4.3
0.199	-956.7	-916.2	40.5	0.202	2.430	-978.0	-944.9	33.1	0.200	5.030	-983.0	-957.7	25.3
0.298	-1083.4	-1163.4	-80.0	0.300	1.790	-1209.6	-1275.5	-65.9	0.301	3.700	-1210.0	-1230.9	-20.9
0.400	-1210.2	-1198.1	12.1	0.400	1.270	-1460.6	-1457.7	2.9	0.401	2.740	-1240.2	-1293.7	-53.5
0.500	-1280.9	-1194.8	86.1	0.501	0.964	-1638.0	-1555.6	82.4	0.500	2.020	-1382.9	-1292.2	90.7
0.600	-1196.2	-1228.9	-32.7	0.630	0.617	-1547.0	-1573.8	-26.8	0.600	1.440	-1262.4	-1297.0	-35.2
0.700	-1149.2	-1198.9	-49.7	0.700	0.466	-1422.4	-1485.2	-62.8	0.700	0.978	-1240.9	-1248.4	-7.5
0.800	-960.0	-916.6	43.4	0.800	0.283	-1198.4	-1151.7	46.7	0.800	0.595	-1008.3	-1003.5	4.8
0.900	-340.2	-346.6	-6.4	0.906	0.906	-552.0	-528.1	23.9	0.900	0.273	-495.0	-495.2	-0.2

15% NaCl					20% NaCl				
x_1	salt concn, wt %	ΔH^{M}_{exp}	ΔH^{M}_{cal}	dev^a	x_1	salt concn, wt %	ΔH^{M}_{exp}	ΔH^{M}_{cal}	dev^a
0.102	10.540	-462.2	-467.4	-5.2	0.101	14.340	-642.1	-643.4	-1.3
0.199	7.780	-884.6	-848.2	36.4	0.210	10.340	-1262.1	-1252.2	9.9
0.299	5.780	-1009.8	-1072.4	-62.6	0.400	5.980	-1389.6	-1453.1	-63.5
0.412	4.150	-1186.2	-1167.6	18.6	0.506	4.350	-1461.6	-1374.7	86.9
0.500	3.170	-1214.2	-1184.5	29.7	0.600	3.190	-1340.4	-1325.2	15.2
0.601	2.260	-1168.6	-1170.2	1.6	0.710	2.080	-1128.2	-1228.8	-100.6
0.711	1.470	-1046.0	-1078.1	-32.1	0.802	1.314	-1048.4	-987.5	60.9
0.800	0.942	-902.2	-883.2	18.9	0.900	0.614	-488.1	-496.1	-8.0
0.900	0.434	-492.1	-494.2	-2.1					

^{a} ($\Delta H^{M}_{cal} - \Delta H^{M}_{exp}$).

Table IX. Heat of Mixing Data for the System Pyridine (1)–Water[†] (2) at 30 °C. Salt: Calcium Chloride

no salt				5% $CaCl_2$				
x_1	ΔH^{M}_{exp}	ΔH^{M}_{cal}	dev^a	x_1	salt concn, wt %	ΔH^{M}_{exp}	ΔH^{M}_{cal}	dev^a
0.095	-357.5	-361.9	-4.4	0.095	3.470	-456.9	-458.1	-1.2
0.199	-956.7	-916.2	40.5	0.200	2.440	-983.9	-978.4	5.5
0.298	-1083.4	-1163.4	-80.0	0.300	1.790	-1379.6	-1369.0	10.6
0.400	-1210.2	-1198.1	12.1	0.400	1.320	-1521.4	-1579.5	-58.1
0.500	-1280.9	-1194.8	86.1	0.500	0.967	-1664.0	-1597.1	66.9
0.600	-1186.2	-1228.9	-42.7	0.602	0.684	-1441.0	-1457.2	-16.2
0.700	-1140.2	-1199.0	-58.8	0.711	0.444	-1192.44	-1206.2	-13.8
0.800	-960.0	-916.6	43.4	0.843	0.214	-842.4	-834.4	8.0
0.900	-340.2	-346.6	-6.4	0.914	0.11	-554.0	-555.7	-1.7

10% $CaCl_2$					15% $CaCl_2$				
x_1	salt concn, wt %	ΔH^{M}_{exp}	ΔH^{M}_{cal}	dev^a	x_1	salt concn, wt %	ΔH^{M}_{exp}	ΔH^{M}_{cal}	dev^a
0.097	7.020	-464.2	-456.7	7.5	0.104	10.470	-512.0	-562.5	-50.5
0.199	5.050	-981.9	-1022.2	-40.3	0.200	7.760	-992.1	-1040.3	-48.2
0.295	3.770	-1421.6	-1403.7	17.9	0.297	5.820	-1440.4	-1409.7	30.7
0.301	3.700	-1448.4	-1421.8	26.6	0.311	5.580	-1468.0	-1444.7	23.3
0.400	2.750	-1562.1	-1596.6	-34.5	0.408	4.200	-1567.6	-1581.9	-14.3
0.500	2.020	-1684.0	-1599.9	84.1	0.541	2.780	-1602.4	-1550.0	52.4
0.618	1.353	-1412.0	-1458.3	-46.3	0.620	2.110	-1421.1	-1460.9	-39.8
0.702	0.970	-1216.4	-1291.7	-75.3	0.710	1.480	-1230.4	-1301.6	-71.2
0.800	0.595	-1082.6	-1013.5	69.1	0.800	0.942	-11149.7	-1048.5	66.2
0.915	0.253	-512.4	-521.3	-8.9	0.911	0.790	-536.2	-544.9	-8.7

^{a} ($\Delta H^{M}_{cal} - \Delta H^{M}_{exp}$).

Table X. Heat of Mixing Data for the System Pyridine (1)–Water[†] (2) at 30 °C. Salt: Zinc Chloride

no salt				5% $ZnCl_2$					10% $ZnCl_2$				
x_1	ΔH^{M}_{exp}	ΔH^{M}_{cal}	dev^a	x_1	salt concn, wt %	ΔH^{M}_{exp}	ΔH^{M}_{cal}	dev^a	x_1	salt concn, wt %	ΔH^{M}_{exp}	ΔH^{M}_{cal}	dev^a
0.095	-357.5	-361.9	-4.4	0.096	3.460	-596.2	-595.0	-0.8	0.097	7.020	-612.4	-610.5	1.9
0.199	-956.7	-916.2	40.5	0.200	2.450	-848.4	-830.9	17.5	0.200	5.030	-852.0	-846.2	5.8
0.298	-1083.4	-1163.4	-80.0	0.298	1.800	-1008.1	-1060.2	-52.1	0.301	3.700	-1028.4	-1091.9	-63.5
0.400	-1210.2	-1198.1	12.1	0.400	1.320	-1320.7	-1300.2	20.5	0.401	2.740	-1412.1	-1340.4	71.7
0.500	-1230.9	-1194.8	36.1	0.500	0.967	-1474.2	-1407.0	67.2	0.500	2.020	-1506.3	-1471.1	35.2
0.600	-1196.2	-1228.2	-32.7	0.601	0.687	-1282.1	-1318.4	-36.3	0.610	1.390	-1368.1	-1393.2	-25.1
0.700	-1140.2	-1198.9	-58.7	0.701	0.464	-1044.0	-1096.7	-53.7	0.700	0.978	-1112.0	-1196.5	-84.5
0.800	-960.0	-916.6	43.4	0.811	0.265	-888.4	-842.3	46.1	0.805	0.578	-999.5	-930.9	68.6
0.900	-340.2	-346.6	-6.4	0.900	0.129	-623.6	-632.9	-9.3	0.901	0.244	-614.2	-624.4	-10.2

^{a} ($\Delta H^{M}_{cal} - \Delta^{M}_{exp}$).

in which the heat of mixing was expressed as a power series in $(x_1 - x_2)$ as follows:

$$\Delta H^{M}_{x} = x_1 x_2[A_0 + A_1(x_1 - x_2) + A_2(x_1 - x_2)^2 + ...] \quad (1)$$

where x_1 and x_2 are the mole fractions of components 1 and 2 respectively and A's are constants which are functions of temperature and system properties. Tsao and Smith (*9*), Klinkenberg (*12*), Rowlinson (*13*), and a number of other in-

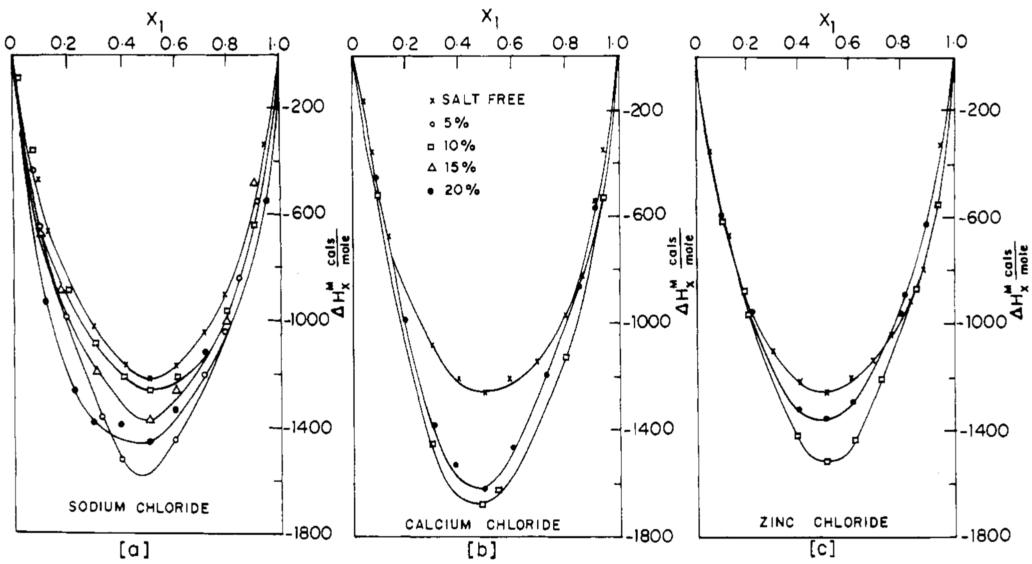


Figure 5. Effect of salt on heat of mixing. System: pyridine (1)-water (2). (a) NaCl; (b) $CaCl_2$; (c) $ZnCl_2$. Temperature 30 °C. x_1 = mole fraction of pyridine. Concentration of salt (in wt %) in water before mixing.

Table XI. Constants in the Heat of Mixing Equation (Eq 1) at 30 °C

system		A_0	A_1	A_2	A_3	A_4	av err %[a]
methanol (1)–water (2)	salt-free	−757.8	−513.8	−485.7	−7.4	−62.1	0.487
	5% NaCl	−635.6	431.4	−241.9	−196.2	−239.0	2.387
	10% NaCl	−547.9	354.6	−218.5	−151.7	224.3	3.419
	15% NaCl	−487.2	392.7	102.5	−95.8	16.6	3.538
	20% NaCl	−364.9	−345.4	−110.2	−106.2	233.0	2.352
	5% $CaCl_2$	1256.1	−735.4	39.1	−540.9	1401.0	3.300
	10% $CaCl_2$	1097.5	−1014.0	1189.2	−75.3	−234.0	5.240
	5% $ZnCl_2$	−811.2	311.2	−181.5	58.9	−627.5	1.541
	10% $ZnCl_2$	−774.7	259.7	−623.9	13.4	−395.6	1.868
methanol (1)–benzene (2)	salt-free	683.9	−269.0	74.3	−767.1	1113.1	4.988
	5% NaCl	645.9	−202.1	−40.0	−893.1	984.4	4.561
	5% $CaCl_2$	829.8	−73.9	143.9	−876.1	1357.3	3.203
	10% $CaCl_2$	945.2	−33.5	271.2	−819.6	1553.6	3.148
	15% $CaCl_2$	1012.2	146.8	−441.0	−1022.6	1959.1	5.229
	5% $ZnCl_2$	843.3	−279.9	−153.7	−946.7	1522.2	3.580
pyridine (1)–water (2)	salt-free	−4779.1	−363.2	−7456.2	1048.8	13315.1	4.447
	5% NaCl	−6219.5	−1358.0	−3280.6	680.5	6715.4	3.439
	10% NaCl	−5168.7	−10.0	−6091.9	−641.5	9525.1	3.073
	15% NaCl	−4737.9	−71.8	−3220.3	−258.7	3655.4	2.910
	20% NaCl	−5515.1	1354.0	−7183.8	−592.1	9311.7	4.591
	5% $CaCl_2$	−6388.5	1392.2	1440.6	−3667.1	−1625.8	1.989
	10% $CaCl_2$	−6399.4	1262.1	−756.8	−3293.9	2250.2	3.867
	15% $CaCl_2$	−6312.5	1053.1	−1934.1	−3043.9	3714.7	3.862
	5% $ZnCl_2$	−5628.1	−201.9	4598.0	60.3	−10292.4	3.599
	10% $ZnCl_2$	−5884.5	−764.1	4360.2	737.0	−9845.1	4.455

[a] This denotes the average error obtained in the calculation of the heat of mixing by eq 1 using these constants.

vestigators have represented their data using two-constant to six-constant equations depending upon the dissymmetry of the system.

In this investigation, various salt systems of differing dissymmetry have been encountered (Figures 3–5). Therefore, a five-constant equation was used to represent the heat of mixing data of these salt-containing systems. The constants were evaluated by use of a high-speed computer by the method of least squares. The values of the constants for each of the systems are given in Table XI.

These constants were used to calculate the values of the heat of mixing for the above three systems using eq 1, and these are given in Tables II–X along with the corresponding experimental values and individual error analysis for each system and salt. It is seen that the minimum and maximum average error percent are as follows: In the methanol-water system they are 0.48 and 5.24; in the methanol-benzene system, 3.15 and 5.23; and in the pyridine-water system, 1.99 and 4.59.

Discussion

It is well-known that alcohols are associated by hydrogen bonding. When alcohols are mixed with components like benzene, they dissociate, implying hydrogen bond breaking. Since energy must be absorbed to produce this dissociation, systems in which no counterbalancing occurs are expected to be endothermic (*14*). This is the case of the system methanol-benzene-sodium chloride salt. The opposite tendency is observed for calcium chloride and zinc chloride salts which tend toward more complex formation on mixing by exhibiting more exothermicity. As far as the methanol-water system is concerned, the breaking of hydrogen bond occurs when the salts sodium chloride and zinc chloride are used, thus decreasing the exothermic nature of the system. The hydrogen bond breaking is sudden, large, and total when the salt calcium chloride is used, which results in the system nature changing instantaneously from exothermicity to endothermicity. It has been observed that for the pyridine-water system the exothermic values

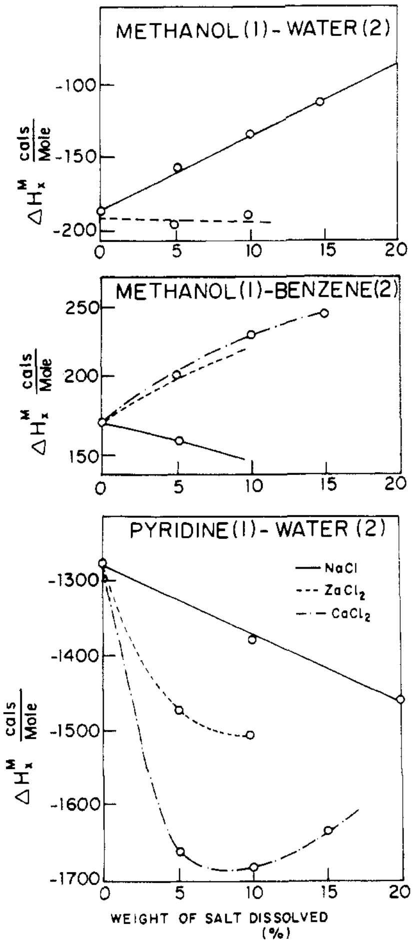


Figure 6. Effect of salts on equimolal concentration.

have increased when all three salts are used. This can be attributed to the further strengthening of hydrogen bonding in the presence of dissolved salts.

Conclusion

In conclusion it can be stated that like relative volatility of solvent in VLE and selectivity of a solute in liquid-liquid equilibria, the enthalpy change on mixing of two solvents is also likely to be influenced by the addition of salts to solvent mixtures. As mentioned earlier, this work has been mainly of an exploratory nature.

Glossary

ΔH_x^M	heat of mixing, cal/mol
V	potential drop across the heating coil, V
I	current passing through the heating coil, A
t	time, s
x_i	liquid-phase composition of component i, mole fraction
A_0, A_1, A_2, ...	binary constants in Scatchard model (eq 1)
1, 2	components 1 and 2

Abbreviations

VLE	vapor-liquid equilibria
LLE	liquid-liquid equilibria

Registry No. NaCl, 7647-14-5; $CaCl_2$, 10043-52-4; $ZnCl_2$, 7646-85-7; MeOH, 67-56-1; benzene, 71-43-2; pyridine, 110-86-1.

Literature Cited

(1) Furter, W. F.; Cook, R. A. *J. Heat Mass Transfer* **1967**, *10*, 23.
(2) Furter, W. F. In *Extractive and Azeotropic Distillation*; Furter, W. F., Ed.; Advances in Chemistry Series 115; American Chemical Society: Washington, DC, 1972; pp 35–45.
(3) Long, F. A.; McDevit, W. F. *Chem. Rev.* **1952**, *51*, 119.
(4) Long, F. A.; McDevit, W. F. *J. Am. Chem. Soc.* **1952**, *74*, 1773.
(5) Furter, W. F. In *Thermodynamic Behavior of Electrolytes in Mixed Solvents*; Furter, W. F., Ed.; Advances in Chemistry Series 155; American Chemical Society: Washington, DC, 1976; pp 26–35.
(6) Sada, E.; Morisue, T.; Miyahara, K. *J. Chem. Eng. Data* **1975**, *20*, 283.
(7) Tomkins, R. P. T.; Gerhardt, G. M.; Lichtenstein, L. M.; Turner, P. J. In *Thermodynamic Behavior of Electrolytes in Mixed Solvents*; Furter, W. F., Ed.; Advances in Chemistry Series 155; American Chemical Society; Washington, DC, 1976; pp 297–302.
(8) Timmermans, J. *Physico-Chemical Constants of Pure Organic Compounds*; Elsevier: New York, 1959.
(9) Tsao, C. C.; Smith, J. M. *Chem. Eng. Prog., Symp. Ser.* **1953**, *49*, 107.
(10) Murti, P. S.; van Winkle, M. *AIChE J.* **1957**, *3*, 517.
(11) Scatchard, G.; Ticknov, L. B.; Goates, J. R.; McCartney, E. R. *J. Am. Chem. Soc.* **1952**, *74*, 3721.
(12) Klinkenberg, A. *Trans. Faraday Soc.* **1937**, *33*, 158.
(13) Rowlinson, J. S.; Thacker, R. *Trans. Faraday Soc.* **1954**, *50*, 1036.
(14) Mrazek, K. V.; VanNess, H. C. *AIChE J.* **1961**, *7*, 190.

Received for review February 18, 1988. Revised April 18, 1989. Accepted July 11, 1989.

Liquid-Liquid Equilibrium Data for the System Water-Benzonitrile-Methanol

Gustavo J. Botto,[†] **Horacio H. Agarás,**[‡] **and Carlos M. Marschoff**[*,†,§]

Departamento de Ingeniería Química, Facultad de Ingeniería, and Departamento de Industrias, Facultad de Ciencias Exactas y Naturales, Universidad de Buenos Aires, Pabellón de Industrias, Ciudad Universitaria, 1428 Buenos Aires, Argentina

Liquid-liquid equilibrium data for the system water-benzonitrile-methanol have been obtained at several temperatures by employing gas chromatography for chemical analysis. The obtained results show that there is no association of methanol molecules in benzonitrile.

Nonaqueous solvents are of increasing importance in industrial processes. Among them, nitriles play a very significant role because of their outstanding physicochemical properties (large dielectric constant, low vapor pressure, good electrochemical stability) and, also, because they intervene in a number of reactions, particularly in regard to the obtention of pharmaceutical drugs.

Economical use of nitriles in industry requires efficient ways for their recovery, and since in a number of cases distillation is not useful, or might even be dangerous, alternative separation processes must be considered. Solvent extraction seems to be a reasonable choice, but the lack of data on ternary equi-

---

[†] Departamento de Ingeniería Química.
[‡] Departamento de Industrias.
[*] Author to whom correspondence should be addressed.
[§] Member of the Carrera del Investigador Científico, Comisión de Investigaciones Científicas de la Provincia de Buenos Aires.

0021-9568/89/1734-0382$01.50/0 © 1989 American Chemical Society