Table III. $E^{\circ}_{Ca(Hg)}$ Values

Temp., ° C	$E^{\circ}_{Ca(Hg)}$, Volts
25	−1.9974 (±0.0004)
40	−2.0065 (±0.0006)
55	−2.0111 (±0.0007)
70	−2.0213 (±0.0006)

may be observed when approaching the upper limit of $CaCl_2$ molalities used here ($0.1m$). One can infer, therefore, that in the case of such uni-bivalent electrolytes as $CaCl_2$ Guggenheim's expression can still be used, as a practical simplification, with good success up to ≅0.1 mole per kg.

The $E^{\circ}_{Ca(Hg)}$ values obtained over the temperature range of experiment are collected in Table III, and can be represented by least-squares Equation 9,

$$E^{\circ}_{Ca(Hg)} = -1.97129 + (2.75163 \times 10^{-4})\, T - (1.22225 \times 10^{-6})\, T^2 \quad (9)$$

where T is the absolute temperature, with a mean deviation of fit of 1 mv, which is of the same order as the experimental uncertainty. The present $E^{\circ}_{Ca(Hg)}$ value at 25° C substantiates the value $E^{\circ}_{Ca(Hg)} = -1.996 \pm 0.001$ volts as recalculated by Butler (*2*) from Drucker and Luft's (*6*) results.

Once the $E^{\circ}_{Ca(Hg)}$ and $dE^{\circ}_{Ca(Hg)}/dT$ values are known, the latter taken from the first derivative of Equation 9, the standard thermodynamic functions G°, H°, and S° for the calcium amalgam can be determined. Referring to the amalgam electrode reaction,

$$Ca^{2+} + 2\, e \rightarrow Ca(Hg) \quad (10)$$

for which $\Delta G^{\circ} = -2FE^{\circ}_{Ca(Hg)}$, $\Delta S^{\circ} = 2FdE^{\circ}_{Ca(Hg)}/dT$, $\Delta H^{\circ} = -2E^{\circ}_{Ca(Hg)}F + 2FTdE^{\circ}_{Ca(Hg)}/dT$, one gets at 25° C $G^{\circ}_{Ca(Hg)} = -40.06$ kcal $mole^{-1}$, $H^{\circ}_{Ca(Hg)} = -43.88$ kcal $mole^{-1}$, $S^{\circ}_{Ca(Hg)} = -2.9$ cal deg^{-1} $mole^{-1}$. The data for the aqueous Ca^{2+} ion, required by Equation 10, were taken from the standard literature (*21*).

As the $S^{\circ}_{Ca^{2+}}$ value at 25° C in the literature (*21*) is referred to the convention $S^{\circ}_{H^+} = 0$ at all temperatures, a correction of 2 × 15.605 cal deg^{-1} $mole^{-1}$ has been applied to make the value of $S^{\circ}_{Ca^{2+}}$ consistent with the convention $E^{\circ}_{H^+/H_2} = 0$ at all temperatures, which in turn implies that $S^{\circ}_{H^+} = \frac{1}{2}\, S^{\circ}_{H_2} = 15.605$ cal deg^{-1} $mole^{-1}$ at 25° C (*14*).

LITERATURE CITED

(1) Bates, R.G., Bower, V.E., *J. Res. Nat. Bur. Stand.* **53**, 282 (1954).
(2) Butler, J.N., *J. Electroanal. Chem.* **17**, 309 (1968).
(3) Butler, J.N., *J. Phys. Chem.* **68**, 1828 (1964).
(4) Butler, J.N., Huston, R., *Ibid.*, **71**, 4479 (1967).
(5) Butler, J.N., Huston, R., Hsu, P.T., *Ibid.*, **71**, 3294 (1967).
(6) Drucker, C., Luft, F., *Z. Physik. Chem.* **121**, 307 (1926).
(7) Fosbinder, R.J., *J. Amer. Chem. Soc.* **51**, 1345 (1929).
(8) Guggenheim, E.A., *Phil. Mag.* **19**, 588 (1935).
(9) Harned, H.S., *J. Amer. Chem. Soc.* **51**, 416 (1929).
(10) Harned, H.S., Owen, B.B., "Physical Chemistry of Electrolytic Solutions," 3rd ed., p. 252, Reinhold, New York, 1958.
(11) *Ibid.*, p. 490.
(12) *Ibid.*, p. 548.
(13) Hückel, E., *Physik. Z.* **26**, 93 (1925).
(14) Ives, D.J.G., Janz, G.J., "Reference Electrodes," pp. 13, 14, Academic Press, New York, 1961.
(15) *Ibid.*, pp. 204, 207.
(16) Lewis, G.N., Randall, M., "Thermodynamics," 2nd ed. rev. by K.S. Pitzer and L. Brewer, pp. 246, 247, 258, McGraw-Hill, New York, 1961.
(17) Lingane, J.J., "Electroanalytical Chemistry," 2nd rev. ed., p. 91, Interscience, New York, 1958.
(18) *Ibid.*, p. 123.
(19) MacInnes, D.A., Cowperthwaite, I.A., *J. Amer. Chem. Soc.* **53**, 555 (1931).
(20) Meites, L., "Handbook of Analytical Chemistry," 1st ed., Sec. 3, pp. 169, 170, 1963.
(21) Natl. Bur. Stand. (U.S.), "Selected Values of Chemical Thermodynamic Properties," Circ. **500**, 386 (1952).
(22) Robinson, R.A., Stokes, R.H., "Electrolyte Solutions," 2nd rev. ed. pp. 200, 201, Butterworths, London, 1965.
(23) *Ibid.*, p. 231.
(24) *Ibid.*, p. 497.
(25) Shedlovsky, T.A., *J. Amer. Chem. Soc.* **72**, 3680 (1950).
(26) Shibata, F.L.E., *J. Sci. Hiroshima Univ.* **A1**, 147–57 (1931).
(27) Tamele, M., *J. Phys. Chem.* **28**, 502 (1924).

RECEIVED for review March 9, 1970. Accepted July 7, 1970. Investigation carried out with financial support from Ente Nazionale Idrocarburi, Rome, Italy, through its branch S.N.A.M. Progetti.

Effect of Organic and Inorganic Salts on Relative Volatility of Nonaqueous Systems

GLENN W. LINDBERG[1] and DIMITRIOS TASSIOS
Newark College of Engineering, Newark, N. J. 07102

The components of some liquid binary solutions may be either impossible or difficult to separate by normal distillation owing to the existence of an azeotrope or a very small relative volatility. Often the desired separation can be achieved by the technique of extractive distillation in which a third component, the extractive agent, is added to the solution. The extractive agent enhances the relative volatility of the close boiling compounds or it destroys the azeotrope.

The majority of work in the field of extractive distillation has dealt with the addition of an organic liquid component as the extractive agent. However, extractive distillation can also be carried out by utilizing soluble salts as the separating agent in aqueous solution (*1, 3*). If the dissolved salt can selectively form a liquid phase association complex with one of the two components present, the volatility of this component will be reduced. The net effect will be to enhance the volatility of the second component, said to be "salted out" with respect to the first. Also, the salting out effect depends on the radius and charge of the ions; it increases with increasing charge and decreasing radius of the ion (*2*).

Although the effect of salts on the relative volatility of the components of aqueous solutions has been studied rather extensively, essentially no work has been done in the area of nonaqueous solutions, probably owing to the

---

[1] Present address, Merck & Co., Inc., Rahway, N. J. 07065.

The effect of one organic salt, CH_3COOK, and one inorganic salt, LiBr, on the vapor-liquid equilibrium of nonaqueous systems *n*-hexane–ethanol and hexene-1–ethanol at 60° C was investigated. Even though the effect of the salts on the relative volatility of the hydrocarbon-ethanol binaries is significant, the azeotropes are not destroyed and the relative volatility of the hexane-hexene pair is not appreciably improved, mainly because of the limited solubility of the salts in the hydrocarbon rich phases.

very small solubility of salts in hydrocarbons which represent the majority of the cases where extractive distillation is applied.

This study will consider the effect of salts on the relative volatility of the constituents of nonaqueous solutions. Vapor-liquid equilibrium data for the systems *n*-hexane–ethanol and hexene-1–ethanol with various salt concentrations of potassium acetate and lithium bromide were obtained to determine the effects of the presence of a dissolved salt on the vapor-liquid equilibrium of a nonaqueous system; the effect of the size of the radii of the salts ions on the relative volativity of the solution components; and the feasibility of employing solutions of salts in ethyl alcohol as extractive distillation agents for the separation of the *n*-hexane–hexene-1 pair, and salts for the hydrocarbon-ethyl alcohol separation.

SELECTION OF SYSTEMS

The hydrocarbons *n*-hexane and hexene-1 were selected as they represent a typical case where extractive distillation could be applied. Also they differ only by one double bond, and therefore any differences in vapor-liquid equilibrium behavior could be related to the double bond. Ethanol was chosen as a solvent because it forms azeotropes with the two hydrocarbons and is also a relatively good solvent for salts. These materials had a boiling range that permitted equilibrium data to be collected at reasonable pressures in glass apparatus.

Potassium acetate and lithium bromide were selected as salts because of a relatively high degree of solubility in the hydrocarbon-alcohol mixture. Also the effect of the ionic radii, which has been shown to be important in aqueous solutions, could be studied because of the markedly different sizes of the ions.

EXPERIMENTAL

Materials. The *n*-hexane and hexene-1 used in this experimental work were obtained from Phillips Petroleum Co. as the pure grade 99.0 mole % minimum purity. The hydrocarbons were assayed by gas chromatography, exceeded 99.5 mole % purity, and were used without further purification.

The ethanol, obtained from U.S. Industrial Chemicals as 200 proof with a minimum purity of 99.9 volume %, was used without further purification.

Anhydrous reagent grade potassium acetate and lithium bromide, each with a minimum assay of 99.0% purity, were used. These hygroscopic salts were dried under heat and vacuum to achieve a moisture content of less than 0.1% by Karl Fisher assay.

Table I summarizes some of the physical properties of the compounds employed.

Apparatus and Method. A modified Ellis still (*6*) was used throughout the investigation for the determination of the vapor-liquid equilibrium data. A three-liter ballast tank was connected between the equilibrium still and the manostat to minimize any fluctuations in pressure. Temperature measurement was accomplished by the use of two mercury-in-glass thermometers which were standardized against a National Bureau of Standards mercury-in-glass thermometer. The pressure was measured by utilizing an open-end mercury manometer and a cathetometer. The atmospheric pressure was measured by a Fortin type mercury barometer that could be read with a vernier to 0.1 mm. The temperature in the still was maintained at 60° ± 0.05° C by adjustment of the pressure.

The liquid and vapor phases were analyzed on an Aerograph Model A-90-P2 gas chromatograph connected to an Inflotronics CRS 11 HSP/42A electronic integrator. The column used consisted of 50- to 80-mesh Poropak Q packed in a 5-foot section of 1/4-inch o.d. stainless steel tubing.

Experimental Results. Vapor-liquid equilibrium data at 60° for the systems *n*-hexane–ethanol and hexene-1–ethanol were taken with and without the presence of the salts so the effect of the salts could be determined. The liquid phase activity coefficient was calculated from Equation 1 (*13*):

$$\ln \gamma_i = \ln \frac{y_i P}{x_i P_i'} + \frac{(B_{ii} - V_i^L)(P - P_i')}{RT} + \frac{P\delta_{12} y_2^2}{RT} \qquad (1)$$

In the presence of salts, salt-free compositions were employed. The second virial coefficients and the interaction virial coefficient were estimated from the correlations of O'Connell and Prausnitz (*10*). The obtained values of B_{ii} in cc per gram mole are: *n*-hexane, −1400.1; hexene-1, −1325.0; and ethanol, −1438.2. The values obtained for δ_{12} in cc per gram mole are −940.6 for the *n*-hexane–ethanol mixture and −921.1 for the hexene-1–ethanol mixture. The values for *n*-hexane and hexene-1 agree with those developed by Hanson (*7*) from PVT data. The obtained corrections for the activity coefficients due to vapor phase imperfections were small, no more than 5.5%, as expected at such low pressure.

The results were tested for thermodynamic consistency by using the Redlich-Kister area test (*11*). The plot of $\ln(\gamma_i/\gamma_2)$ *vs.* x_1 should yield two areas, one above and one below the x axis, that are nearly equal for isothermal systems, if the data are consistent. The function γ_1/γ_2 was fitted by least squares to the empirical relationship:

$$\ln(\gamma_1/\gamma_2) = A_0 + A_1(x_1 - 0.5) + A_2(x_1 - 0.5)^2 \qquad (2)$$

A consistency index, defined by Hanson (*7*) as

$$CI = \frac{I_p + I_n}{|I_p| + |I_n|} \qquad (3)$$

Table I. Physical Properties of the Materials

Property		Ethanol	*n*-Hexane[a]	Hexene-1[b]
Molecular wt.		46.07	86.17	84.16
Refractive Index, 25° C	Exptl.	1.3611	1.3722	1.3851
	Lit.	1.3611	1.3723	1.3850
B.P. 760 mm	Exptl.	. . .	68.75	63.51
	Lit.	78.3	68.74	63.49
Vapor Press., 65° C	Exptl.	439.2	. . .	. . .
	Lit.	438.4[c]	. . .	. . .

[a] Data from (*4*). [b] Data from (*5*). [c] Data from (*12*).

where I_p is the positive integrated area and I_n the negative integrated area, was used to express the consistency of the data.

Tables II and III present the experimental vapor-liquid equilibrium data for the systems studied along with the calculated activity coefficients. The consistency index values are also included, in the cases where sufficient experimental points for its evaluation were available.

The effect of the salts and their amounts on the vapor-liquid equilibrium behavior of the systems *n*-hexane–ethanol and hexene-1-ethanol are shown in Figures 1 and 2 respectively. The dependence of the relative volatility of hexene to hexane on the salt amount is presented in Figure 3.

Table II. *n*-Hexane–Ethanol Data at 60° C

x_1	y_1	P, mm	γ_1	γ_2
		No Salt		
0.133	0.548	698.1	4.960	1.005
0.238	0.608	770.0	3.367	1.079
0.336	0.636	778.2	2.562	1.186
0.453	0.653	794.7	1.965	1.374
0.548	0.662	807.8	1.642	1.601
0.665	0.670	801.5	1.387	2.153
0.772	0.678	805.6	1.206	3.067
0.881	0.695	791.9	1.077	5.546
		C.I. = 0.087		
		1.5 Mole % Potassium Acetate		
0.336	0.648	813.3	2.655	1.154
0.449	0.660	815.9	2.037	1.352
0.551	0.667	818.8	1.678	1.623
		2.9 Mole % Potassium Acetate		
0.136	0.600	749.5	5.664	0.946
		5.4 Mole % Potassium Acetate		
0.134	0.603	744.9	5.771	0.937
		4.5 Mole % Lithium Bromide		
0.136	0.621	780.7	6.084	0.928
		9.0 Mole % Lithium Bromide		
0.132	0.682	785.2	6.922	0.780

Table III. Hexene-1–Ethanol Data at 60° C

x_1	y_1	P, mm	γ_1	γ_2
		No Salt		
0.128	0.546	715.7	4.479	1.032
0.221	0.613	813.7	3.232	1.079
0.325	0.654	855.6	2.491	1.184
0.424	0.674	877.9	1.992	1.315
0.527	0.687	894.8	1.653	1.550
0.647	0.700	878.4	1.376	2.011
0.753	0.713	873.2	1.206	2.757
0.859	0.732	863.4	1.076	4.469
		C.I. = 0.062		
		1.5 Mole % Potassium Acetate		
0.229	0.641	841.0	3.387	1.050
0.327	0.660	871.0	2.521	1.174
0.426	0.680	881.7	2.201	1.311
0.537	0.694	887.5	1.647	1.563
		2.9 Mole % Potassium Acetate		
0.120	0.579	751.9	5.059	0.999
		5.4 Mole % Potassium Acetate		
0.128	0.595	756.2	5.132	0.964
		4.5 Mole % Lithium Bromide		
0.132	0.623	807.3	5.511	0.948
		9.0 Mole % Lithium Bromide		
0.133	0.691	849.6	6.394	0.817

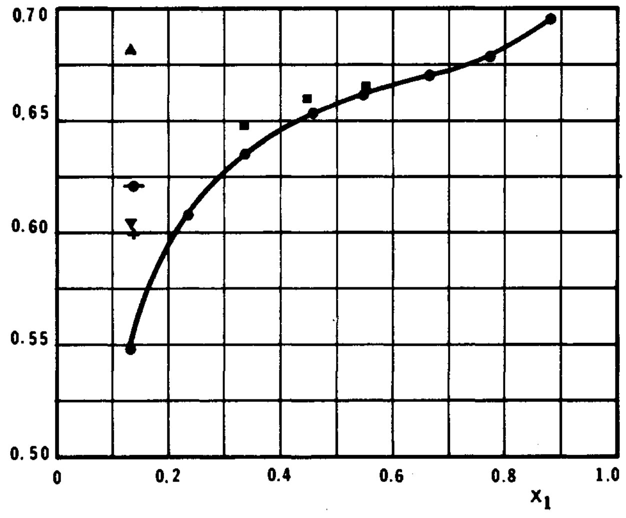

Figure 1. Salt effect on vapor-liquid equilibrium. System: *n*-hexane–ethanol, T = 60° C

- ● No salt
- ■ 1.5% potassium acetate
- + 2.9% potassium acetate
- ▼ 5.4% potassium acetate
- -●- 4.5% lithium bromide
- ▲ 9.0% lithium bromide

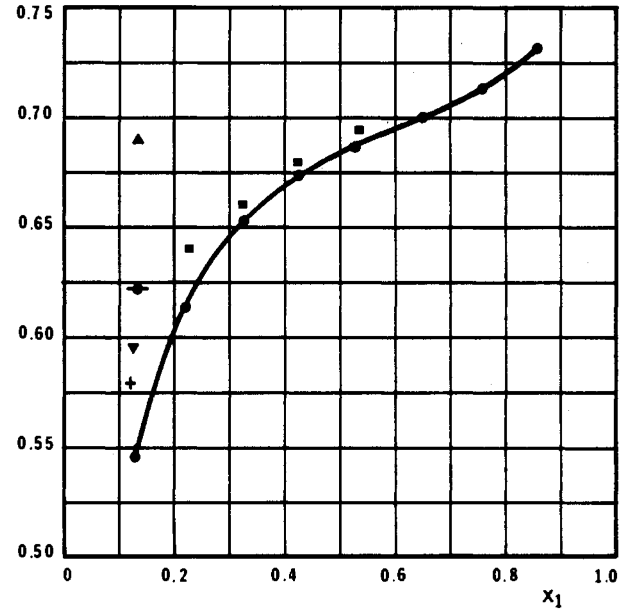

Figure 2. Salt effect on vapor-liquid equilibrium. System: hexene-1–ethanol, T = 60° C

- ● No salt
- ■ 1.5 potassium acetate
- + 2.9% potassium acetate
- ▼ 5.4% potassium acetate
- -●- 4.5% lithium bromide
- ▲ 9.0% lithium bromide

DISCUSSION AND CONCLUSIONS

The above experimental results can be explained by considering the types of forces that are exerted between ethanol and salts and between hydrocarbons and salts. Owing to

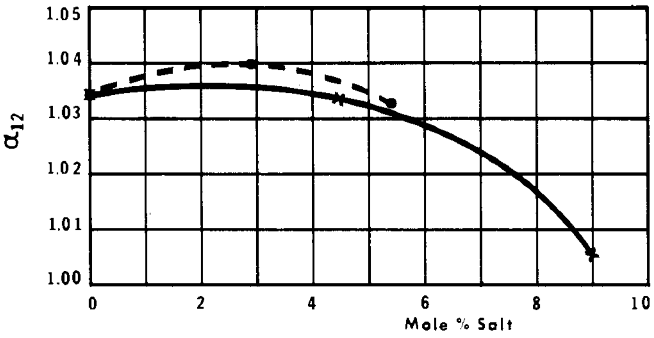

Figure 3. Effect of salt concentration on the relative volality. System: hexene-1–n-hexane with ethanol (83.5%), T = 60° C

● potassium acetate
× lithium bromide

the relatively large dipole moment of ethanol, strong electrostatic forces develop between the salt ions and the charge centers of the ethanol. Since n-hexane has no dipole moment and hexene-1 has only a slight one, the interaction forces are much weaker and are essentially owing to dispersion forces. Therefore, one would expect the salts to be more soluble in ethanol than in the hydrocarbons. Indeed, this is a well-known fact. The dissolution of a salt in the hydrocarbon-ethanol mixture should result in the association of more ethanol molecules than hydrocarbon molecules to the salt and there should be an increased hydrocarbon concentration in the vapor phase over the salt-containing binary system (Figures 1 and 2). Also, increased salt concentrations should enhance the salting out effect (Figures 1, 2, and 3).

Since the electrostatic field of an ion increases with decreasing ion radius, salts containing ions of smaller radius should have a greater salting out effect than those containing ions of larger diameter (Figures 1, 2, and 3). The effect of LiBr is larger than that of CH_3COOK since Li^+ < K^+ and Br^- < CH_3COO^-. The point of 2.9% of CH_3COOK is considered in error. Similar observations were made in aqueous solutions by Johnson and Furter (*8, 9*), Ciparis and Smorigaite (*2*) and others. In general, the rule of increasing salting out effect with decreasing ion radius can be considered as a useful guide (*9*).

Finally, because of the presence of the double bond and the slight dipole moment of hexene-1 as opposed to a zero dipole moment for n-hexane, the interaction between the salt and hexene-1 should be larger. This should bring about a decrease of the relative volatility of hexene-1 with respect to n-hexane (Figure 3).

On the basis of the results presented in Figure 3, alcohol solutions of the two studied salts cannot be employed as extractive agents since the azeotropes are not destroyed. As expected, the presence of the salt solution tends to invert the relative volatility of hexene-1 to n-hexane. However, the impact is very small bringing the relative volatility close to unity. This is owing to the low solubility of the two salts in alcohol; also ethyl alcohol itself is a very poor extractive solvent for the hydrocarbon pair studied. The key to the employment of salts as extractive agents lies with salts of larger solubility in all constituents of the mixture. Finally, because of the limited salt solubility, neither of the alcohol-hydrocarbon azeotropes was eliminated as seen in Figures 1 and 2.

NOMENCLATURE

A_0, A_1, A_2 = constants in Equation 2
B_{ii} = second virial coefficient of component i, cc/gmole
P = total pressure, atm
P_i' = vapor pressure of ith component, atm
T = temperature, ° K
V_i^L = volume of ith component, pure liquid, cc/gmole
x = salt-free basis mole fraction, liquid
y = mole fraction, vapor
γ = activity coefficient
δ_{12} = interaction coefficient, Equation 1, cc/gmole

Subscripts

i = component i
1 = component 1, the hydrocarbon constituent
2 = component 2, ethanol

LITERATURE CITED

(1) Bogart, M.J.P., Brunjes, A.S., *Chem. Eng. Prog.* **44**, 95 (1948).
(2) Ciparis, J., Smorigaite, N., *Zh. Obshch. Khim.* **34** (12), 3867 (1964).
(3) Cook, R.A., Furter, W.F., *Can. J. Chem. Eng.* **46**, 119 (1968).
(4) Dreisbach, R.R., *Advan. Chem. Ser.* **22**, 19 (1959).
(5) *Ibid.* **22**, 229 (1959).
(6) Ellis, S.R.M., Froome, B.A., *Chem. Ind.* **73**, 237 (1954).
(7) Hanson, D.O., Van Winkle, M., J. CHEM. ENG. DATA, **12**, 319 (1967).
(8) Johnson, A.I., Furter, W.F., *Can. J. Chem. Eng.* **34**, 413 (1957).
(9) *Ibid.* **38**, 78 (1960).
(10) Prausnitz, J.M., Eckert, C.A., Orye, R.V., O'Connell, J.P., "Computer Calculations for Multicomponent Vapor-Liquid Equilibria," Prentice Hall, Englewood Cliffs, N. J., 1967.
(11) Redlich, O., Kister, A.T., *Ind. Eng. Chem.* **40**, 345 (1948).
(12) Scatchard, G., Raymond, C.L., *J. Amer. Chem. Soc.* **66**, 365 (1938).
(13) Van Ness, H.C., "Classical Thermodynamics of Non-Electrolytic Solutions," MacMillan, New York, 1964.

RECEIVED for review March 9, 1970. Accepted July 31, 1970.