In the case of 1-butanol and butyl acetate, butyl acetate has a greater selectivity towards the solute than 1-butanol. However, a study of Figure 6 indicates that 1-butanol is a better solvent than butyl acetate because of its high distribution coefficients.

NOMENCLATURE

Xcw = weight fraction of solute in water-rich phase
Xww = weight fraction of water in water-rich phase
Xcs = weight fraction of solute in solvent-rich phase
Xss = weight fraction of solvent in solvent-rich phase
Xc = weight fraction of solute
Xw = weight fraction of water
Xs = weight fraction of solvent

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Isothermal Vapor-Liquid Equilibrium Data for the Systems Heptane–1-Propanol at 75° C. and Decane–1-Butanol at 100° C.

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Isothermal equilibrium vapor and liquid composition measurements have been made for the heptane–1-propanol system at 75° C. and the decane–1-butanol system at 100° C. Liquid phase activity coefficients were calculated from the equilibrium data and checked for both internal and over-all thermodynamic consistency. Composition-molar volume data were also obtained for both systems at 20° C.

BOTH isothermal and isobaric vapor-liquid equilibrium data for a number of paraffin-alcohol systems have been published (*1*, *9*), but the available information is still far from complete. A thorough literature search indicates that isothermal equilibrium data are lacking on the heptane–1-propanol system in the vicinity of 75° C. and the decane–1-butanol system in the vicinity of 100° C. Data for these systems have been obtained and their thermodynamic consistencies have been checked. Composition–molar volume data at 20° C. have also been obtained for the two systems.

EXPERIMENTAL EQUIPMENT AND PROCEDURE

A detailed description of the experimental equipment, calibrations, procedures, and methods has been given by Lodl and Scheller (*6*).

Briefly, a modification of the vapor recirculation type equilibrium still described by Hipkin and Myers (*3*) was used in this work. Pressure in the still was controlled by a Cartesian manostat of the type described by Gilmont (*2*) and was measured with a mercury manometer to ±0.1 mm. Temperature was measured with an iron-constantan thermocouple and a Leeds and Northrup Type K-2 potentiometer to ±0.1° C. Compositions of equilibrium samples were obtained from molar volume measurements made with the aid of calibrated pycnometers of the type described by Lipkin *et al.* (*5*). The over-all precision of these composition analyses is about ±0.2 mole % (*4*). Molar volume–composition data for each of the systems at 20° C. are contained in Table I.

Table I. Composition–Molar Volume Measurements at 20° C

Mole Fraction, Heptane	Molar Volume, Cc./G.-Mole
HEPTANE–1-PROPANOL SYSTEM	
0.000	74.7
0.084	80.7
0.201	90.1
0.265	95.3
0.314	98.4
0.356	101.4
0.520	113.5
0.654	122.3
0.756	129.9
0.887	138.7
1.000	146.5
Mole Fraction, Decane	
DECANE –1-BUTANOL SYSTEM	
0.000	91.5
0.053	97.2
0.181	110.5
0.330	126.1
0.383	131.6
0.648	159.3
0.720	166.3
0.758	170.3
0.823	176.9
1.000	194.9

The heptane and decane were obtained from Matheson, Coleman, and Bell and had boiling ranges of 98-99° and 173-175° C., respectively. The 1-propanol was Fischer Scientific Co.'s certified reagent grade with a boiling range of 96.9-97.3° C. The 1-butanol was Mallinckrodt Chemical's analytical reagent grade with a 2° C. boiling range. No analyses were made to check the supplier's specifications.

DISCUSSION OF RESULTS

Table II contains the experimental x, y, P equilibrium data for the heptane-1-propanol system at 75° C. and the decane-1-butanol system at 100° C. Figures 1 and 2 are plots of these data.

Liquid phase activity coefficients for the components have been calculated from Equation 1 assuming that the vapor phase behaves as an ideal gas at the low experimental pressures ($P_r < 0.04$).

$$\gamma_i = \frac{y_i P}{x_i P_i^0} \qquad (1)$$

The calculated activity coefficients are tabulated in Table II. Figure 3 is a plot of the activity coefficients for the heptane-1-propanol system at 75° C. A plot of the decane and 1-butanol activity coefficients at 100° C. is not shown here, but is similar in shape to Figure 3.

Table II. Experimental Vapor-Liquid Equilibrium Measurements and Calculated Activity Coefficients

x_1	y_1	P, Mm. of Hg	$\ln\gamma_1$	$\ln\gamma_2$
		Heptane(1)-1-Propanol(2) at 75° C.		
0.000	0.000	297.9	...	0.000
0.020	0.075	348.3	1.292	0.073
0.037	0.145	388.9	1.446	0.122
0.045	0.180	398.4	1.491	0.113
0.060	0.218	424.4	1.455	0.145
0.078	0.275	442.6	1.476	0.129
0.094	0.305	467.9	1.442	0.161
0.108	0.338	486.5	1.448	0.167
0.138	0.370	502.4	1.326	0.183
0.163	0.402	517.2	1.268	0.190
0.207	0.420	541.6	1.119	0.259
0.320	0.470	549.2	0.810	0.337
0.356	0.463	552.3	0.692	0.411
0.375	0.480	550.0	0.674	0.404
0.565	0.550	547.4	0.395	0.617
0.510	0.540	548.8	0.482	0.522
0.660	0.570	538.9	0.260	0.802
0.820	0.640	516.6	0.116	1.218
0.860	0.655	506.6	0.072	1.407
0.880	0.685	497.4	0.076	1.452
0.905	0.710	483.1	0.055	1.574
0.970	0.785	446.1	0.006	2.348
1.000	1.000	361.5	0.000	...
		Decane(1)-1-Butanol(2) at 100° C.		
0.000	0.000	375.0	...	0.000
0.010	0.020	386.1	2.350	0.019
0.025	0.040	385.0	2.124	0.011
0.033	0.039	384.3	1.819	0.018
0.045	0.045	385.0	1.654	0.026
0.048	0.047	384.7	1.632	0.027
0.096	0.062	380.7	1.205	0.052
0.127	0.082	380.0	1.203	0.064
0.153	0.093	376.5	1.133	0.072
0.215	0.106	371.7	0.911	0.121
0.284	0.122	364.0	0.753	0.174
0.312	0.142	359.8	0.799	0.179
0.375	0.140	354.0	0.584	0.262
0.398	0.156	350.7	0.624	0.271
0.563	0.163	334.3	0.270	0.531
0.650	0.190	319.5	0.237	0.679
0.680	0.225	315.1	0.347	0.710
0.780	0.212	292.8	0.077	1.028
0.845	0.220	273.4	0.343	1.300
0.870	0.232	278.1	0.007	1.477
1.000	1.000	73.7	0.000	...

Compositions (±0.2%) were obtained from molar volume measurements using calibrated pycnometers described by Lipkin *et al.* (5).

Over-all and local checks of the thermodynamic consistency of the experimental data have been made. The method of Redlich and Kister (7) was used to check the over-all thermodynamic consistency. Since the specific volume, composition data at 20° C. indicate that the volume change on mixing for both systems is zero, this is assumed also to be so at 75° and 100° C. Thermodynamic consistency requires for a binary system:

$$\int_{x_1=0}^{x_1=1} \ln\frac{\gamma_1}{\gamma_2}\, dx_1 = 0 \qquad (2)$$

Equation 2 may be expressed as two integrals where x_1^0 is the value of x_1 at which $\ln(\gamma_1/\gamma_2) = 0$

$$\int_{x_1=0}^{x_1=x_1^0} \ln\frac{\gamma_1}{\gamma_2}\, dx_1 = \int_{x_1=1}^{x_1=x_1^0} \ln\frac{\gamma_1}{\gamma_2}\, dx_1 \qquad (3)$$

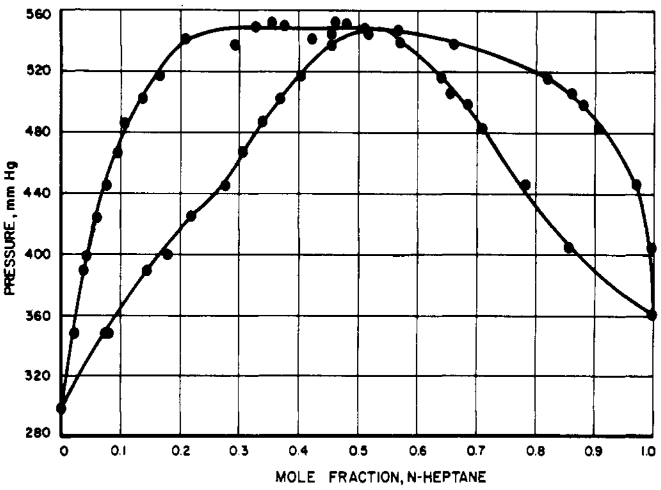

Figure 1. Pressure-composition relationship for heptane-1-propanol at 75° C.

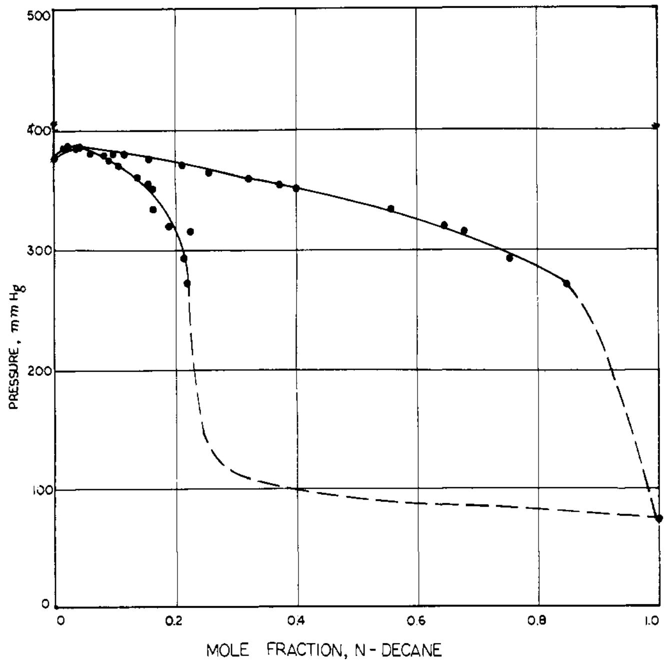

Figure 2. Pressure-composition relationship for decane-1-butanol at 100° C.

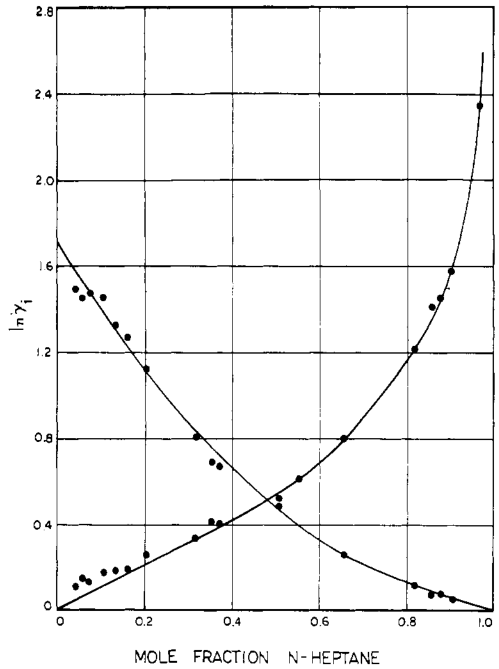

Figure 3. Liquid phase activity coefficients for heptane–1-propanol at 75° C.

For the heptane–1-propanol system at 75° C., the integral on the left side of Equation 3 is about 12.5% smaller than the integral on the right. For the decane–1-butanol system at 100° C., the integral on the left side is 8.2% smaller than the one on the right. Figure 4 shows $\ln(\gamma_1/\gamma_2)$ plotted against x_1 for the decane–1-butanol system. The appearance of this graph is similar to the one for the heptane–1-propanol system.

Tao (*8*) has suggested an integral method for checking the local consistency using the relationship:

$$\Delta Q = Q(x_{1b}) - Q(x_{1a}) = \int_{x_{1a}}^{x_{1b}} \ln\frac{\gamma_1}{\gamma_2}\,dx_1 \tag{4}$$

where

$$Q(x_1) = x_1\ln\gamma_1 + x_2\ln\gamma_2 \tag{5}$$

Figure 4 is a graph of x_1 *vs.* Q calculated from the experimental data and

$$\int_{x_{1a}}^{x_{1b}} \ln\frac{\gamma_1}{\gamma_2}\,dx_1$$

calculated from a smoothed plot of x_1 *vs.* $\ln(\gamma_1/\gamma_2)$. This figure indicates good local consistency of the decane–1-butanol data and is also typical of the heptane–1-propanol system.

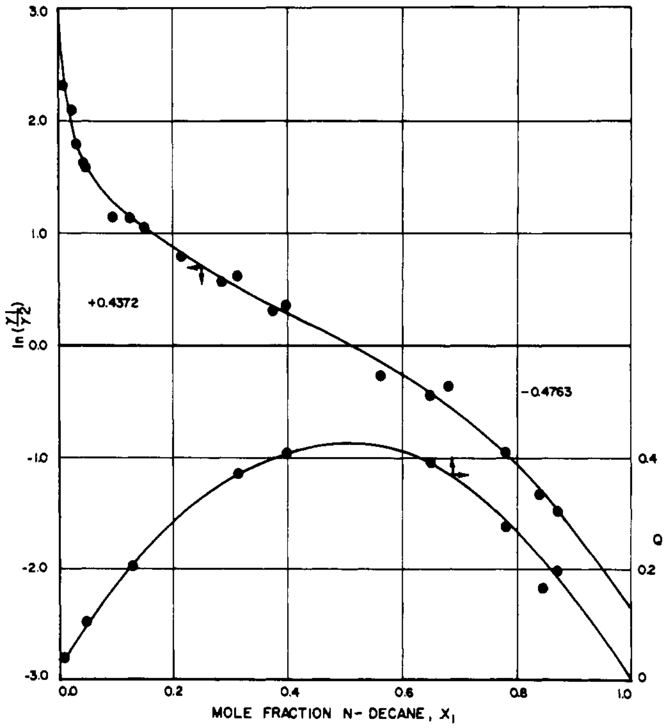

Figure 4. Thermodynamic consistency check for the decane –1-butanol data at 100° C.

NOMENCLATURE

P = total pressure
P_i^0 = vapor pressure of pure component i
Q = dimensionless excess free energy of mixing
x_i = mole fraction of component i in the liquid phase
y_i = mole fraction of component i in the vapor phase
γ_i = liquid phase activity coefficient of component i

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