

EXCESS MOLAR VOLUMES AT THE 308.15 K FOR CONSTITUENT BINARIES OF n-DECANE, n-DODECANE, 1-DECANOL AND 1-DODECANOL

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Abstract—Excess molar volumes (V_m^E) of constituent binary mixtures of n-decane, n-dodecane, 1-decanol and 1-dodecanol which are the products of liquid phase oxidation of n-paraffins, have been measured experimentally as a function of composition x from density measurements at 308.15 K. The excess molar volumes of n-decane-n-dodecane system have negative deviation from the ideality while that of n-dodecane-1-decanol system have positive deviation. In the other systems, excess molar volume exhibits inversion in sign. Experimental data were successfully correlated with Redlich-Kister polynomial.

Key words: Excess Molar Volume, Surfactant, Density, Dodecane, Sec-fatty Alcohol

INTRODUCTION

Sec-fatty C_{10} - C_{18} alcohols are usually used as intermediates of newly developed pollution-low surfactants. Sec-fatty alcohols could be easily manufactured by liquid phase oxidation of C_{10} - C_{13} n-paraffins. This oxidation products are not only sec-fatty alcohols but also small amount of ketons and relatively large amount of unreacted n-paraffins. Hence the recovery and purification of the desired sec-fatty alcohol products require the separation of these mixtures. If this separation carried out by fractionation, the thermodynamic properties of mixtures and the vapor-liquid equilibria of these systems are indispensable for the development of separation process. Previously, we have determined the isothermal and isobaric vapor-liquid equilibrium data for the dodecane inclusive the binary and ternary systems, which are major products of sec-fatty alcohol manufacturing process [Park et al., 1993; Park and Lee, 1993].

In this study we report the excess molar volumes (V_m^E) at 308.15 K and atmospheric pressure for the constituent binaries of n-decane, n-dodecane, 1-decanol and 1-dodecanol mixture. A digital vibrating-tube densimeter was employed to determine the densities of pure components and the binary mixtures. Experimental V_m^E data were correlated with Redlich-Kister polynomial.

THEORETICAL REVIEW

Accurate representation of the chemical activities in a liquid mixture is essential to the design of fluid phase separation equipment. Attempts to model solution behavior are commonly centered to the excess Gibbs energy of mixing (g^E). But g^E model often fail to predict or correlate the solution behavior. For a better understanding of solution behavior, it is advantageous to examine the excess properties. Excess volumes, V_m^E as a function of mole fraction x can be determined with the densities which were measured easily by means of a digital densimeter. The density determination is based on measuring the period of oscillation of the

sample in a hollow U shaped tube. Apparatus constant K in Eq. (1) was determined by the calibration with two densities known reference components. If doubly distilled water and air were chosen as calibrating reference fluids, the accurate air density could be calculated with the Eq. (2).

$$\rho_{1ref} - \rho_{2ref} = (T_{1ref}^2 - T_{2ref}^2)K \quad (1)$$

$$\rho_{Air} = \frac{0.001293}{(1 + 0.00367t)} \times \frac{P(\text{mmHg})}{760} \quad (2)$$

where ρ is the density, T is the period of oscillation and t is a temperature ($^{\circ}\text{C}$). The subscript ref. means the reference component. The densities of pure components or mixtures are then calculated using the relation

$$\rho = K(T^2 - T_{2ref}^2) + \rho_{2ref} \quad (3)$$

The molar excess volume of mixing V_m^E for the binary mixture is defined as

$$V_m^E = V - x_1V_1 - x_2V_2 \quad (4)$$

where V is the molar volume of the binary mixture, x_i and V_i are the mole fraction and molar volume of pure component i , respectively. So the excess molar volume V_m^E can be calculated by means of Eq. (5) from the experimental densities of the mixture and the pure components.

$$V_m^E = \left[\frac{x_1M_1 + x_2M_2}{\rho_m} \right] - \frac{x_1M_1}{\rho_1} - \frac{x_2M_2}{\rho_2} \quad (5)$$

where ρ_m is the density of binary mixture, and M_i is the molar mass of component i . The Redlich-Kister polynomial function is used to correlate the experimental V_m^E data

$$V_m^E = x_1x_2 \sum_i A_i (x_1 - x_2)^{i-1} \quad (6)$$

where A_i is the correlation constant. Standard deviations of the fits S_d are defined as

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EXPERIMENTAL SECTION

Table 1. Experimental densities (ρ) of pure components with literature data

Chemicals	ρ (g/cm ³)					
	This work	lit.	This work	lit.	This work	lit.
	293.15 K		298.15 K		308.15 K	
n-decane	0.72995	0.7300 ^a			0.71847	-
n-dodecane	0.74863	0.7487 ^a			0.73783	-
1-decanol	0.82973	0.8297 ^a			0.81916	-
1-dodecanol			0.83068	0.8308 ^b	0.82283	-

^a[Weast et al., 1986] ^b[Dean, 1987]

$$S_d = \left[\frac{\sum (V_{calc}^E - V_{exp}^E)_i^2}{(N - n)} \right]^{1/2} \quad (7)$$

where V_{calc}^E is the excess molar volume, which calculated by the Eq. (6) and V_{exp}^E is experimental excess molar volume N is the number of experimental data and n is the number of fitted constant A_i [Choudary and Naidu, 1985; Francesconi and Comelli, 1992].

1. Materials

All chemicals (n-decane, n-dodecane, 1-decanol and 1-dodecanol) were commercial products from Merck (Darmstadt, Germany) of the best grade quality. They were stored over Union Carbide type 0.4 nm molecular sieve (from Fluka) and then used without any further purification because the purity of substance is not a critical factor in V_m^E measurement [Berti et al., 1989; Spanedda, et al., 1991]. After drying, their purities were more than 99.5 wt% by gas chromatographic analysis. The experimental densities of pure components at 293.15 K, 298.15 K and 308.15 K are given in Table 1 along with the values from the literature [Weast et al., 1986; Dean, 1987] for comparison.

2. Preparation of Mixture Sample

Ca. 3.5 ml sample mixture were prepared by weight with precisions of ± 0.1 mg. In order to escape the significant experimental error due to evaporated mass, a 4 ml small glass vial was used as a mixture vessel. The systematic experimental error of mixture concentration were estimated to be less than 1×10^{-4} mole fraction.

3. Density Measurement

Table 2. Experimental densities excess molar volumes of each binary system at 308.15K

X_1	V_m^E (cm ³ /mol)	ρ (g/cm ³)	X_1	V_m^E (cm ³ /mol)	ρ (g/cm ³)	X_1	V_m^E (cm ³ /mol)	ρ (g/cm ³)	X_1	V_m^E (cm ³ /mol)	ρ (g/cm ³)
n-decane-1-decanol						n-dodecane-1-dodecanol					
0.0666	-0.0189	0.81238	0.5484	-0.0342	0.76346	0.0490	-0.0088	0.81862	0.5510	0.0509	0.77542
0.1027	-0.0275	0.80870	0.5982	-0.0204	0.75841	0.0995	-0.0130	0.81428	0.6014	0.0604	0.77112
0.1511	-0.0391	0.80379	0.6476	0.0008	0.75338	0.1576	-0.0144	0.80927	0.6520	0.0723	0.76680
0.2010	-0.0478	0.79871	0.6987	0.0120	0.74824	0.2027	-0.0128	0.80538	0.6989	0.0794	0.76282
0.2510	-0.0577	0.79365	0.7485	0.0275	0.74322	0.2490	-0.0072	0.80139	0.7485	0.0942	0.75859
0.3002	-0.0603	0.78865	0.8011	0.0452	0.73794	0.2973	-0.0023	0.79723	0.7983	0.1055	0.75436
0.3505	-0.0584	0.78353	0.8498	0.0652	0.73304	0.3558	0.0058	0.79220	0.8480	0.1149	0.75016
0.4037	-0.0546	0.77812	0.8979	0.0743	0.72825	0.4521	0.0251	0.78391	0.8861	0.1199	0.74696
0.4495	-0.0483	0.77347	0.9521	0.0710	0.72292	0.4997	0.0391	0.77981	0.9534	0.1062	0.74138
0.5017	-0.0418	0.76818				n-decane-n-dodecane					
n-decane-1-dodecanol						0.0310	-0.0015	0.73732	0.5494	-0.0252	0.72802
0.0717	-0.0591	0.81644	0.5465	-0.1426	0.76980	0.0817	-0.0056	0.73648	0.5929	-0.0251	0.72716
0.1077	-0.0795	0.81316	0.5988	-0.1295	0.76421	0.1388	-0.0101	0.73551	0.6453	-0.0251	0.72612
0.1492	-0.0996	0.80932	0.6980	-0.1029	0.75339	0.2023	-0.0127	0.73441	0.6960	-0.0243	0.72509
0.1975	-0.1215	0.80480	0.7475	-0.0808	0.74784	0.2505	-0.0163	0.73357	0.7482	-0.0232	0.72401
0.2508	-0.1348	0.79969	0.8027	-0.0385	0.74150	0.2995	-0.0184	0.73270	0.7962	-0.0220	0.72300
0.3004	-0.1466	0.79488	0.8488	0.0047	0.73612	0.3506	-0.0207	0.73177	0.8486	-0.0183	0.72187
0.3509	-0.1542	0.78990	0.8979	0.0280	0.73037	0.4011	-0.0221	0.73084	0.9015	-0.0144	0.72071
0.3990	-0.1564	0.78507	0.9534	0.0445	0.72383	0.4523	-0.0242	0.72988	0.9403	-0.0106	0.71984
0.4501	-0.1566	0.77986	0.9907	0.0157	0.71952	0.4973	-0.0249	0.72903	0.9801	-0.0050	0.71893
n-dodecane-1-decanol						1-decanol-1-dodecanol					
0.0429	0.0101	0.81498	0.5029	0.1394	0.77414	0.0499	-0.0234	0.82276	0.5499	0.0032	0.82094
0.0979	0.0244	0.80972	0.5522	0.1485	0.77018	0.1073	-0.0220	0.82257	0.5999	0.0041	0.82075
0.1016	0.0242	0.80938	0.5996	0.1544	0.76644	0.1498	-0.0204	0.82243	0.6487	0.0041	0.82057
0.1527	0.0408	0.80459	0.6510	0.1603	0.76245	0.2028	-0.0175	0.82224	0.6898	0.0039	0.82041
0.2029	0.0540	0.79998	0.6935	0.1629	0.75923	0.2497	-0.0150	0.82208	0.7500	0.0037	0.82017
0.2488	0.0730	0.79581	0.7455	0.2546	0.75534	0.3044	-0.0107	0.82187	0.7995	0.0027	0.81998
0.3011	0.0859	0.79119	0.8018	0.1653	0.75121	0.3501	-0.0072	0.82170	0.8520	0.0020	0.81977
0.3492	0.1052	0.78698	0.8471	0.1627	0.74796	0.4005	-0.0035	0.82151	0.9007	0.0016	0.81957
0.4055	0.1180	0.78220	0.9032	0.1497	0.74403	0.4492	-0.0011	0.82133	0.9508	0.0008	0.81936
0.4496	0.1291	0.77851	0.9449	0.1180	0.74123	0.5006	0.0015	0.82113			
0.4497	0.1284	0.77850									

Table 3. Fitted constants A_i for Eq. (6) and the standard deviations S_d (cm^3/mol)

System	Constants						
	A_1	A_2	A_3	A_4	A_5	A_6	S_d
n-decane-1-decanol	-0.15999	0.42526	0.10519	-0.21286	0.91896	1.08971	0.0034
n-decane-1-dodecanol	-0.59847	0.23345	-0.12966	0.09940	1.09326	1.12617	0.0032
n-dodecane-1-decanol	0.56335	0.39779	0.00012	0.14709	1.02199	0.96070	0.0023
n-dodecane-1-dodecanol	0.15925	0.52159	-0.09522	-0.41988	1.29841	1.74621	0.0043
n-decane-n-dodecane	-0.09901	-0.03252	-0.01193	-0.00486	-0.03423	-0.05188	0.0005
1-decanol-1-dodecanol	0.00319	0.09544	-0.06624	-0.12172	-0.21470	0.39560	0.0014

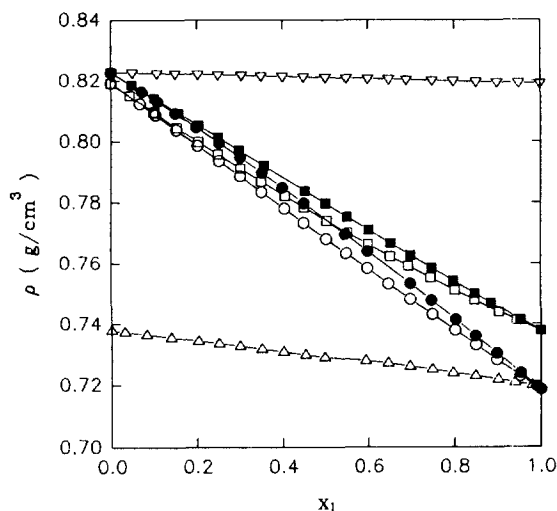


Fig. 1. Measured density ρ at the temperature 308.15 K plotted against mole fraction x_1 ; for \circ ; n-decane(1)-1-decanol(2), \bullet ; n-decane(1)-1-dodecanol(2), and for \square ; n-dodecane(1)-1-decanol(2), \blacksquare ; n-dodecane(1)-1-dodecanol(2), and for \triangle ; n-decane(1)-n-dodecane(2), ∇ ; 1-decanol(1)-1-dodecanol(2).

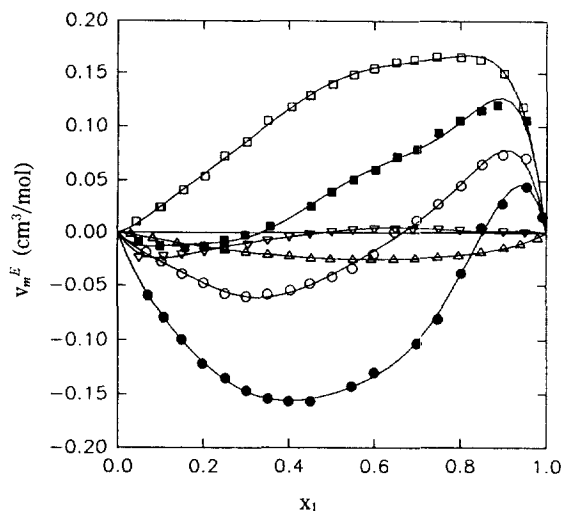


Fig. 2. Excess molar volumes V_m^E at the temperature 308.15 K plotted against mole fraction x_1 . The solid curves are least-squares representation of results by Eq. (6). The same symbols and systems are used as in Fig. 1.

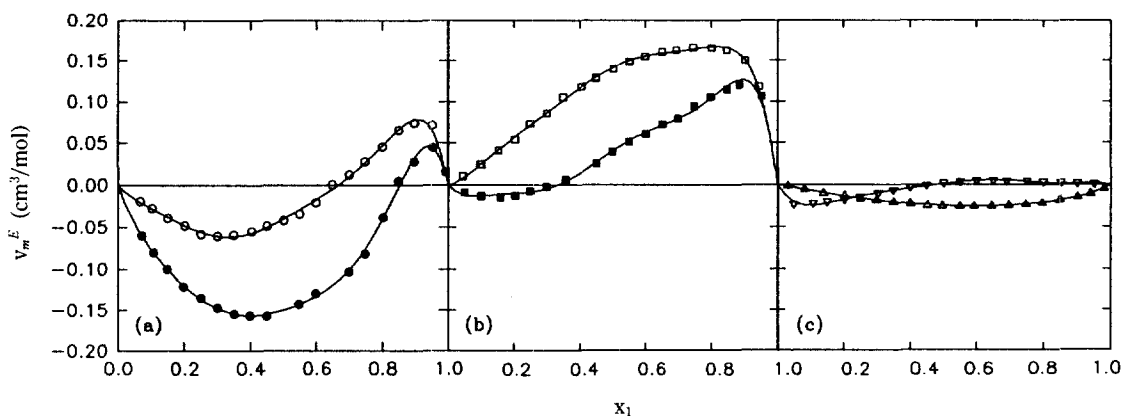


Fig. 3. Excess molar volumes V_m^E at the temperature 308.15 K plotted against mole fraction x_1 . The solid curves are least-squares representation of results by Eq. (6). The same symbols and systems are used as in Fig. 1.

A vibrating tube digital densimeter (Anton-Paar DMA-02D) was employed to determine the densities of the pure components and binary mixtures. The densimeter was calibrated for each measurement by using doubly distilled water and dried air at atmospheric pressure. All the measurements were carried out at atmospheric pressure, and the barometric pressure was measured by means of high precision mercury manometer (Wallace & Tiernan).

The temperature of vibrating tube was regulated by Lauda thermostat of which temperature calibrated against a Hewlett Packard platinum digital resistance thermometer as a accuracy of ± 0.01 K. Measurement time interval, we have chosen 15 min to attain the constant temperature and oscillation period stability. Apparatus and operating procedure are described elsewhere [Letcher and Lucas, 1982; Pettenati et al., 1990].

RESULTS AND DISCUSSION

The densities of the binary mixtures of all composition ranges have been measured at 308.15 K and atmospheric pressure condition. The complete sets of measured density data are reported in Table 2 together with the experimental V_m^E data, calculated by the Eq. (5). Each set of V_m^E results was fitted with the Eq. (6). The values of parameter A, and deviation S_d determined by the method of least squares with all points weighed equally, are reported in Table 3. The results of the density determination are plotted in Fig. 1. The trends of V_m^E with respect to different x_1 are shown in Fig. 2 for all systems experimented with the V_m^E curves predicted from the smoothing equations. The close examination of experimental data and those predicted by empirical polynomials shows that all the predicted V_m^E values that are in qualitative agreement with the measured V_m^E values. Excess volumes, V_m^E changes their sign with composition in all the systems except n-decane-n-dodecane and n-dodecane-1-decanol mixtures. These experimented systems classified arbitrarily as three different binary groups for more easy comparison, represented in Fig. 3.

It can be seen from Fig. 3 that n-decane-1-decanol, n-decane-1-dodecanol and n-dodecane-1-dodecanol mixture systems tend to be sigmoid shaped with contractions and expansions occurring respectively at low and high mole fractions of alkanes. Furthermore, there is a tendency for the magnitudes of deviations from the ideality to increase with increasing difference of the chain length of the components. This is assumed that the volume behavior of experimented alkane-alkanol systems is the resultant of contributions from two opposing effects. A contraction occurs when the alkane can be accommodated interstitially within the hydrogen bonded alcohol structure. on the other hand, an expansion occurs when there is a breakup of the alcohol structure. But n-dodecane-1-decanol mixture in the Fig. 3(b) show only the positive deviation from the ideality. This positive excess volumes suggest that the structure breaking effect of the components is dominant in this binary mixture.

The algebraic values of V_m^E of the n-decane-n-dodecane and 1-decanol-1-dodecanol mixtures [Fig. 3(c)] show an almost ideal volumetric behavior because of their chemical and geometrical similarity.

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